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TECHNICAL PROGRESS REVIEWS

REACTOR FUEL PROCESSING

Prepared for U. S. ATOMIC ENERGY COMMISSION by ARGONNE NATIONAL LABORATORY

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APRIL 1959 VOLUME 2 NUMBER 2

TECHNICAL PROGRESS REVIEWS

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REACTOR FUEL PROCESSING

a review of recent developments *prepared by*

ARGONNE NATIONAL LABORATORY

APRIL 1959 VOLUME 2 NUMBER 2

foreword

This quarterly review of *Reactor Fuel Processing* has been prepared at the request of the U. S. Atomic Energy Commission, Division of Information Services. It is intended to assist those interested in keeping abreast of important developments in this field. In each Review it is planned to cover those particular subjects in which significant new results have been obtained. The Review does not purport to abstract all the literature published on this broad field during the quarter. Instead it is intended to bring each subject up to date from time to time as circumstances warrant.

Usually these reviews do not include foreign literature. In the last issue (Volume 2, Number 1) papers from the Geneva Conference which had become available were covered. In this issue the remaining Geneva papers of interest are included.

Interpretation of results, where given, represents the opinion of the editors of the Review who are personnel of the Argonne National Laboratory, Chemical Engineering Division. Those taking part in the preparation of this issue are L. Burris, Jr., I. G. Dillon, A. A. Jonke, S. Lawroski, M. Levenson, W. J. Mecham, W. A. Rodger, J. H. Schraidt, W. B. Seefeldt, R. K. Steunenberg, and V. G. Trice. The reader is urged to consult the original references for more complete information on the subject reported and for the interpretation of results by the original authors.

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Issued quarterly by the U. S. Atomic Energy Commission. Use of funds for printing this publication approved by the Director of the Bureau of the Budget on November 1, 1957.

REACTOR FUEL PROCESSING

COMMERCIAL ASPECTS OF FUEL PROCESSING

Fuel-cycle Invitation

On Oct. 15, 1958, the AEC invited industry and research institutions to submit proposals to provide services and facilities and to perform research and development on various phases of the fuel cycle.[1] A total of 107 proposals from 39 firms was received.[2] The firms and the number of proposals from each are shown in Table I-1.

Euratom Agreement

An agreement[3] for cooperation in the civil uses of atomic energy between the United States and Euratom was signed in Brussels on Nov. 8, 1958. Although this agreement is primarily directed toward reactor development, two of the provisions are of particular interest to fuel processors:

1. Guarantee for a 10-year period of a market for the plutonium recovered from the power reactors in the program.

2. A long-term assurance by the United States that chemical reprocessing services will be available under terms comparable to those then available to U.S. industry.

Ore Concentrate Purchase Program Modified

On Nov. 21, 1958, the AEC announced that it was modifying the ore concentrate purchase program of May 24, 1956. On that date the Commission announced that it would guarantee the purchase of U_3O_8 in concentrates produced and delivered during the period Apr. 1, 1962, to Dec. 31, 1966, at a price of $8.00 per pound U_3O_8 in an acceptable concentrate. By the modification the Commission withdraws the concentrate purchase program with respect to ore reserves developed after Nov. 24, 1958. For ore reserves developed subsequently the Commission will "make contracts to purchase concentrates to the extent that requirements dictate and on such terms and conditions and at such prices as the Commission may from time to time agree upon."[4]

Table I-1 FIRMS MAKING PROPOSALS UNDER AEC FUEL-CYCLE DEVELOPMENT PROGRAM[2]

Firm	No. of proposals
ACF Industries, Inc., Nuclear Products-Erco Div.	1
Aerojet-General Nucleonics	4
Allied Chemical Corp.	1
AMF Atomics	1
American Metal Products, Inc.	2
American-Standard Atomic Energy Div.	3
Atomic Power Development Associates	1
Associated Nucleonics, Inc.	1
Atomics International	1
Babcock & Wilcox Co.	5
Battelle Memorial Institute	9
The Carborundum Co.	1
Clevite Corp.	2
Combustion Engineering, Inc., Nuclear Div.	8
Cornell Aeronautical Laboratory	5
Denver Research Institute	1
Electric Auto-Lite Co.	1
The Fluor Corp., Ltd.	2
Ford Instrument Co.	1
General Electric Co.	3
W. R. Grace Co.	4
Ionics, Inc.	1
Jones & Laughlin Steel Corp.	1
The Martin Co., Nuclear Div.	12
Mallinckrodt Chemical Works and Clevite Corp.	1
M & C Nuclear, Inc.	2
National Carbon Co.	1
Nuclear Development Corp. of America	3
National Lead Co.	3
Nuclear Materials & Equipment Corp.	1
Nuclear Metals, Inc.	5
Sanderson and Porter	1
Sylvania-Corning Nuclear Corp.	3
TRG, Inc.	1
Tracerlab, Inc.	3
Thor-Westcliffe Research, Inc.	2
Union Carbide Corp.	2
University of Virginia	1
Westinghouse Electric Co.	7

Table I-2 NUCLEAR POWER PLANT FUEL DATA[g]

(The table below is a composite of data presented in two tables in "Survey of Initial Fuel Costs of Large U. S. Nuclear Power Stations," published by the Technical Appraisal Task Force of the Edison Electric Institute.)

Cost factors	Shippingport	Lagoona Beach	Indian Point	Rowe	Dresden
Fuel loading	Seed: 80 kg U, 75 kg U^{235}; U-Zr plates Blanket: 12,900 kg U, 92 kg U^{235}; UO_2 pellets	Core: 1800 kg U, 485 kg U^{235}; U–10 wt.% Mo pins Blanket: 38,720 kg U, 140 kg U^{235}; U rods	950 kg U, 16,850 kg Th, 885 kg U^{235}; ThO_2-UO_2 pellets	21,400 kg U, 642 kg U^{235}; UO_2 pellets	53,600 kg U, 792 kg U^{235}; UO_2 pellets
Average enrichment	Seed: 93% Blanket: 0.7%	Core: 27% Blanket: 0.36%	5%	3%	1.5%
Average residence[a]		Core: 0.3 years Blanket: 2.7 years	2.0 years	1.3 years	3.7 years
Average burn-up[b]	Core: 140,000 Mwd/t Blanket: 2,940 Mwd/t	Core: 9,160 Mwd/t Blanket: 916 Mwd/t	15,200 Mwd/t	6,800 Mwd/t	10,000 Mwd/t
Fuel costs, mills/kw-hr(e):					
Fabrication[c]	26.47	5.42	2.36	3.52	2.20
Reprocessing[d]	1.04	2.55	0.27	0.74	0.53
Working capital[e]	2.70	0.40	0.46	0.42	0.74
Lease charges[f]	0.52	2.46	1.16	0.74	0.40
Replaceable controls and structures[g]	2.13	0.04	0.05	0.08	0.14
Uranium fissioned or lost	2.43	2.67	2.65	2.00	1.45
Plutonium credit[h]	1.81	3.68	None	2.50	1.97
Total	33.48	9.86	6.94	5.00	3.49

[a] Number of years residence in reactor is based on a 0.7 plant factor.

[b] Average burn-up is limited by loss of reactivity to override equilibrium xenon poison at rated operating conditions or by radiation damage to fuel. In the case of the Shippingport station, there is evidence that core and seed burn-up could be substantially greater than shown. Lagoona Beach estimates are based on biweekly changes of part of a core load. The Indian Point station will use multizone enrichment. Uncertainties in the Rowe station estimate reflect the possibility of using multizone enrichment in the first and second cores. Dresden station estimates are based on burn-ups to be achieved by shuffling fuel.

[c] Fuel fabrication costs are based on manufacturers' estimates for the Indian Point, Rowe, and Dresden stations; projections of firm contracts for Lagoona Beach; and recorded costs for Shippingport.

[d] Reprocessing costs are based on announced AEC service charges.

[e] In estimating fuel-cycle working capital costs, it has been assumed that annual cost is 9 per cent of the average working capital required and that the capital required is the equivalent of the fuel fabrication cost of the first core.

[f] Annual fuel material lease cost is 4 per cent of the value of leased uranium in fresh fuel. Fuel material lease costs for the Lagoona Beach and Rowe stations will be waived by AEC for at least part of the initial three years.

[g] The cost of replaceable core structures and controls is highly uncertain.

[h] Plutonium credit is calculated at a value of $30 per gram.

[i] The first Indian Point core will be ThO_2 and fully enriched UO_2. Therefore no plutonium is made and there is no credit. Credit for the U^{233}-U^{235} mixture in spent fuel is included in "uranium fissioned or lost."

Food Irradiation

At a recent meeting of the Grocery Manufacturers of America, Swift & Co., National Biscuit Co. (Nabisco), and Thomas J. Lipton, Inc., noted that they have recently cut back on their research and development efforts in the radiation preservation of their respective food products. Swift's Vice President Harold E. Wilson said that his company has not yet found out how to keep irradiated meat from having an unpleasant odor. Nabisco President George H. Coppers stated that, in addition to the problem of odor and unpleasant taste, irradiated products cannot be browned. Lipton's chairman, R. B. Smallwood, said his company was not making progress in its studies on the effects of radiation on soups.[5]

EEI Survey of Initial Fuel Costs

The report of the Edison Electric Institute's technical appraisal task forces on nuclear power entitled "A Survey of Initial Fuel Costs of Large Nuclear Power Stations" was recently published. In it are contained nuclear power plant fuel data from four commercial power reactor stations and the Shippingport plant. These data are summarized[6] in Table I-2. In the large commercial water-cooled nuclear power plants (Indian Point, Rowe, and Dresden), nominal fuel-cycle cost estimates range from 3½ to 7 mils per electrical kilowatt hour. This assumes plutonium is worth $30 per gram. Using $12 instead of $30 per gram for plutonium results in an increase of 1 to 2 mils per electrical kilowatt hour in fuel-cycle cost.

The report analyzes the relative importance of the elements of fuel-cycle cost. Assuming a plutonium credit of $12 per gram, approximately 45 per cent of the total fuel cost is assigned to fabrication, 15 per cent for spent fuel processing, 15 per cent for net fuel material cost, 10 per cent for fuel material lease cost, 10 per cent for fuel-cycle working capital cost, and 5 per cent for the cost of replaceable core controls and structures.

References

1. *Reactor Fuel Processing*, Vol. 2, No. 1, January 1959.
2. AEC Receives 107 Proposals to Participate in Fuel Cycle Development Program, AEC Press Release A-329, Dec. 11, 1958.
3. U.S.-Euratom Agreement for Cooperation Signed, AEC Press Release A-301, Nov. 8, 1958.
4. Uranium Ore Concentrate Purchase Modification, AEC Press Release A-312, Nov. 24, 1958.
5. *The Forum Memo to Members*, Atomic Industrial Forum, Inc., Vol. 5, No. 12, December 1958.
6. *The Forum Memo to Members*, Atomic Industrial Forum, Inc., Vol. 6, No. 2, February 1959.

For the second time in six months a serious criticality accident occurred while handling aqueous solutions of fissionable material. This accident occurred at Los Alamos on Dec. 30, 1958, during plutonium recovery operations and it resulted in the death of one employee.[1]

One step in the plutonium recovery operating procedure requires addition of nitric acid to an emulsion containing plutonium solids and solution in diluted form. The following information on the incident is based on a preliminary investigation. After placing the emulsion in the tank, the operator was believed to have added a dilute plutonium solution from a second tank. Solids containing plutonium were probably washed from the bottom of the second tank with nitric acid and the resultant mixture of nitric acid and plutonium-bearing solids added to the tank containing the emulsion. Shortly after starting the stirrer motor to initiate an expected mild nonnuclear reaction between the emulsion and the acid, the operator observed a "blue flash," which was also observed by a second employee in an adjoining room. Both also reported hearing a "noise." The operator, who during the interim had fallen to the floor, got up and turned off the agitator. A few seconds later, perhaps in the belief that the blue flash had been caused by an electrical short circuit or other nonnuclear phenomenon, he was understood to have again pressed the starter button. After hearing what was later described as a rumbling noise, he ran out of the building where he told a second employee: "I am burning up." Perhaps because of an incorrect belief that the "burning" feeling had resulted from acid exposure, the employee was led to a shower. In doing this, they passed the "emulsion" tank where the second employee shut off the stirrer motor. The employee died 35 hr later from the effects of a radiation exposure tentatively estimated at 12,000 rem (plus or minus 50 per cent).

Two employees (other than the operator) received radiation exposures ranging up to 118 rem. These employees were not seriously injured. Property damage was reported as negligible.

A thorough study and evaluation is being made of all factors in the accident. This will be made public when it becomes available.

Reference

1. AEC Serious Accident Bulletin 143, Jan. 27, 1959.

The large number of proposed reactor designs and resulting variety of fuel types require a variety of processes for dissolution and pretreatment before processing. Developments in "head-end" mechanical and chemical processing are presented.

Mechanical Processing

For many of the proposed fuels it would be desirable to remove the cladding material mechanically. Mechanical processing offers the important advantages of smaller aqueous waste volumes, the use of less corrosive reagents for dissolving the fuel material when the difficult-to-dissolve cladding is removed, and increased plant capacity in the absence of dissolved cladding material to process streams.

In work at Hanford[1] initial tests with a 40-ton hydraulic shear using straight knives to chop simulated fuel elements (porcelain-filled stainless-steel tubing bundles) showed that:

1. A 150-ton capacity shear would be required for chopping the largest known power reactor fuel element (N.S. *Savannah*) without first making smaller subassemblies.
2. Closure of chopped segment ends is more a function of element core material and shear blade velocity than cutting pressure.
3. "Fine-size" chopping (less than 1-in. segments) of large cross-section bundles is not practical.

By using a 40-ton hydraulic shear[2] equipped with type 420 stainless-steel V shear blades and by cutting both simulated fuel elements and stainless rod and bar, it was shown that:

1. Shear power requirements nearly doubled, but shear operation is smoother for V blades as compared to straight blades.
2. The expected life of 420 stainless steel would be approximately half that of a hardened high carbon steel blade.

By using a straight moving knife and a V stationary knife, cutting tubular and solid stainless steel and simulated reactor fuel assemblies (ceramic-filled stainless-steel tube bundles) indicated that:

1. Shear forces required for the V straight blade combination are intermediate (about 15,000 lb/sq in. for the ceramic bundles) between those required for all straight blades (10,000 lb/sq in.) and those required for all V blades (19,000 lb/sq in.).
2. Shear forces for rod bundles or tubes are predictable from shear equations used for solid stock.

Chemical Dejacketing

Selective chemical dissolution of fuel jackets and structural components is an attractive alternate to mechanical dejacketing or complete dissolution. The fuel cores thus exposed can be dissolved by another reagent in a second step. The principal jacket materials are aluminum, zirconium or Zircaloy, and stainless steel.

Removal of Zirconium and Zircaloy Jackets

The rate of dissolution of zirconium and Zircaloy-2 in mixtures of nitric and hydrofluoric acid has been examined[3] at the Idaho Chemical Processing Plant (ICPP). At 40°C and 0.5*M* initial hydrofluoric acid concentration, zirconium dissolved in nitric–hydrofluoric acid mixtures at an initial rate of approximately 6 mg/(sq cm)(min) over a nitric acid range of 0*M* to 13*M*. Data on the effect of initial hydrofluoric acid concentration on dissolution rates for zirconium and Zircaloy-2 at 115°C are also given. Similar data for zirconium have been obtained at Brookhaven.[4] The latter are summarized in Figs. 1 and 2. A flow sheet for removing Zircaloy-2 cladding from a uranium oxide core (Commonwealth Edison fuel) by dissolution in hydrofluoric acid to a F/Zr ratio of 4.5 was reported by ORNL.[5]

A Zirflex flow sheet[6] is being applied to decladding of Zircaloy-clad aluminum-plutonium fuel elements proposed for the Plutonium Recycle Test Reactor (PRTR) at Hanford. Using

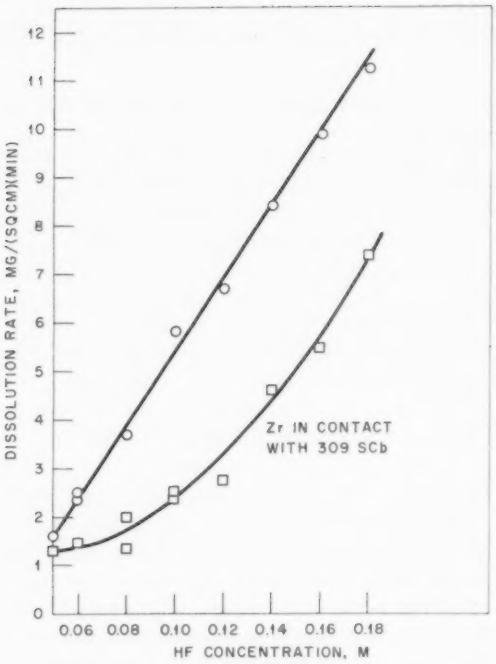

Figure 1—Dissolution rate of reactor-grade zirconium in 2.5M nitric acid as a function of hydrofluoric acid concentration, refluxing.[4]

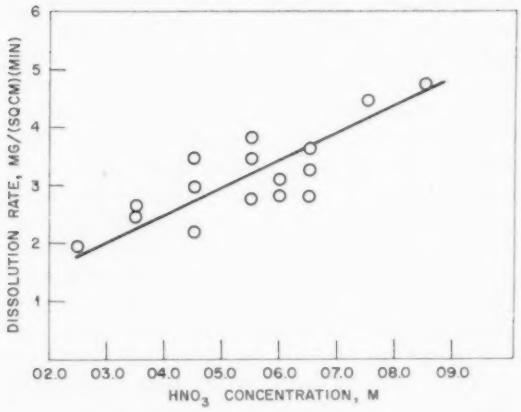

Figure 2—Dissolution rate of reactor-grade zirconium in 0.06M hydrofluoric acid as a function of nitric acid concentration, refluxing.[4]

Zircaloy-clad aluminum-uranium elements as a stand-in for the aluminum-plutonium elements, after 4 hr[2] uranium waste losses amounted to 0.25 per cent. The rods were bare and clean when removed from the decladding solution.

In several Zirflex flow sheet demonstration experiments at ORNL[7] with oxidized unirradiated PWR blanket fuel specimens, the uranium loss to the decladding solution was less than 0.08 per cent and did not vary systematically with the decladding time. The uranium loss to the nitric acid–insoluble residue was less than 0.005 per cent in nearly every case. In similar experiments using unirradiated Experimental Boiling Water Reactor (EBWR) and Submarine Thermal Reactor (STR) fuel, as much as 95 per cent and 85 per cent, respectively, of the ammonium fluoride dissolvent have been recycled. The percentages of uranium in the recycle streams were 0.4 and 2 per cent, respectively.

Removal of Stainless-steel Jackets

The Sulfex process[6] has been proposed for removal of the type 304L stainless-steel jackets from the Yankee Atomic Power Reactor (YAPR) fuel elements (uranium oxide) and from Consolidated Edison fuel elements (96 per cent thorium dioxide–4 per cent uranium oxide). At ORNL[7] all major parts of the flow sheet for the decladding of Consolidated Edison fuel with 6*M* sulfuric acid and the subsequent dissolution of the core in 13*M* nitric acid–0.04*M* sodium fluoride–0.04*M* aluminum nitrate have now been demonstrated on a laboratory scale. It has been shown that the presence of stainless-steel corrosion products (5 g/liter) in the initial sulfuric acid dissolver solution results in a reduction of the initial rate of dissolution of 304L stainless steel from about 5 to 0.01 mg/(sq cm)(min) in 4*M* sulfuric acid and from about 12 to 0.02 mg/(sq cm)(min) in 6*M* sulfuric acid.

Additional Hanford data[8] support those reported previously[6] to indicate that irradiated uranium oxide dissolves more rapidly in sulfuric acid than does nonirradiated oxide. Irradiated uranium oxide (~500 g/ton) dissolved in boiling 4*M* sulfuric acid at a rate 100 times that observed in the same system for unirradiated uranium oxide, either as powder or as sintered and machined cylinders.

Studies of reactions[8] between dilute sulfuric acid and uranium and uranium dioxide in a Co^{60} gamma-radiation field disclosed that:

1. Uranium metal dissolves to yield only uranium(IV) while a mixture of uranium(IV) and uranium(VI) is produced from uranium oxide.

2. The G value* for oxidation of uranium(IV) to uranium(VI) in a 4*M* sulfuric acid, 0.01*M* to 0.02*M* uranium, is about unity at room temperature and 90°C.

Dissolution

Simultaneous Dissolution of Jacket and Core

1. Zirconium Fuel Elements. Two of the more promising methods for dissolution of zirconium-containing fuel elements are the use of aqueous fluoride–nitric acid mixtures and hydrochlorination (Zircex process). Experiments at Savannah River with reactor fuel material consisting of a zirconium-clad alloy containing 90 wt.% uranium and 10 wt.% molybdenum have been continued,[9] with the objective of codissolving the cladding and core material in nitric acid containing a low concentration of fluoride ion. If a concentration of hydrofluoric acid less than 0.1*M* proves to be sufficient to dissolve the zirconium cladding at a suitable rate, stainless-steel equipment such as 309 Nb may be used without excessive corrosion.

The Zircex process has been discussed in previous reviews,[6,10,11] and work continues on this process at Oak Ridge.[7,12,13] A flow sheet for this process is shown in Fig. 3.

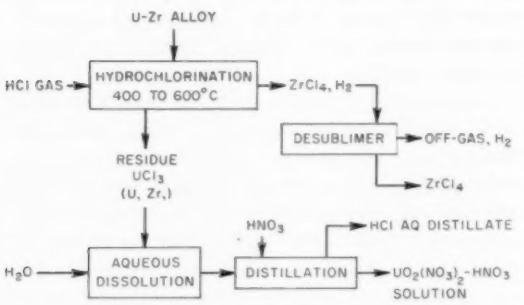

Figure 3—Zircex process flow sheet.[13]

One of the limitations of the Zircex process to date is the loss of uranium which is carried off with the volatile zirconium tetrachloride. Since the ratio of uranium to zirconium in a fuel element may be quite small (<1 per cent), a large percentage loss of uranium can be caused by small concentrations of uranium in the zirconium tetrachloride sublimate. For example, 1 mg of uranium in 1000 mg of zirconium tetrachloride in the desublimator may result in a uranium loss of more than 20 per cent. The uranium loss should desirably be kept below 1 per cent if the Zircex process is to be adapted to industrial-scale reprocessing.

In six runs made at ORNL,[12] the total uranium loss with the volatile zirconium tetrachloride was 7 to 17 per cent. The hydrochlorination of a small piece of an STR subassembly with essentially pure hydrogen chloride (0.02 mole % oxygen, 0.01 mole % carbon dioxide) resulted in a uranium loss of 1.9 per cent as nitric acid insoluble material in the uranium chloride residue.[9] The result of this single test indicated that the use of pure hydrogen chloride alone will not ensure the reduction of insoluble uranium losses to an acceptable value.

2. Stainless-steel Fuel Elements. Promising proposed methods of dissolution of fuel elements containing stainless steel include dissolution in dilute aqua regia (Darex process) and in dilute sulfuric acid (Sulfex process). Another proposed method is dissolution in nitric acid–hydrofluoric acid mixtures.

A flow sheet for the Darex process was given in the first Review of this series.[10] Present work at Oak Ridge is directed toward carrying out this process on a continuous basis.[14,15] In 39 runs carried out in a continuous pot dissolver, dissolution rates varied from 10 to 50 mg/(sq cm)(min) for type 304 stainless steel and stainless steel–uranium oxide alloy (5.5 to 11 per cent uranium oxide) with aqua regia feed streams composed of nitric acid–hydrochloric acid ratios of 5 to 2, 5 to 1.5, 3 to 2, and 3 to 1.5.

Darex processing is also being considered at Hanford.[1,2,8] Pilot-plant operations included the sequential dissolution of stainless steel and uranium dioxide. Type 304 stainless-steel 32-mil tubing was dissolved smoothly and completely in 1.25*M* hydrochloric acid–2*M* nitric acid in 2 to 3 hr. The resultant solution was butted with nitric acid and used for three separate dissolutions of sintered or compacted uranium dioxide. Complete dissolution of ½-in.-thick pieces of sintered uranium dioxide was obtained in 7, 5, and 4 hr at nitric acid concentrations of 1.5*M*, 3*M*, and 4*M*, respectively. The hydrochloric acid concentration was in the range

*G = number of molecules of product produced per 100 ev energy absorbed in system.

of 1*M* to 1.2*M*, and the terminal uranium concentration was 0.3*M*.

The chloride concentration of the dissolver effluent was reduced from 1.25*M* (~35,000 ppm) to 50 ppm by a four-step procedure: (1) concentrate the feed by a factor of 2, (2) add a volume of 60 per cent nitric acid equal to the volume of the original feed, (3) boil under reflux for 3 hr, and (4) concentrate to one-fifth of the original volume. Chloride removal is not affected markedly by the presence of uranium.

Subsequent to the stainless-steel dissolution in another run, two consecutive charges of solid 8-in. uranium slugs were dissolved in the Hanford pilot plant. The uranium dissolution rates were 180 mils/hr for the first charge and 25 to 30 mils/hr for the second. Laboratory studies later indicated that the nitrate-to-chloride mole ratio must be below about 4 in order to obtain high dissolution rates. The nitrate-to-chloride mole ratios were 2.4 and 5.2 for the first and second pilot-plant runs.

Two stainless-steel test dissolutions were made in the Darex pilot-plant unit to demonstrate the depassivating effect of copper. In both runs, a piece of copper was placed upon the stainless-steel charge. The dissolution step was then interrupted, a procedure that previously has caused passivation. Upon reheating with sufficient excess chloride present in solution, the remaining stainless steel in contact with the copper dissolved. In one run, a piece of stainless-steel tubing suspended in the solution above the copper and the rest of the charge was only partially dissolved.

3. Aluminum Fuel Elements. A proposed fuel for the PRTR at Hanford is an aluminum-silicon-plutonium alloy. The insoluble residues produced during the dissolution of such an alloy were investigated[16] with respect to particle size, shape and distribution, composition, and surface-active tendencies. The samples studied contained from 0.4 to 7.0 wt.% silicon (the high analysis represents a cast base aluminum-silicon alloy). They were dissolved in mercury-catalyzed nitric acid. Two types of solid residue were produced. One was a finely divided brown material, and the other was a black crystalline material relatively large in size. Only the black crystalline material was obtained when cast aluminum-silicon was dissolved in nitric acid. Spectrographic analysis of the residues showed that silicon and aluminum were the major constituents. X-ray diffraction analysis of each type indicated the presence of elemental silicon only. Removal of the residue from process solutions with sintered stainless-steel filters was possible, but 90 per cent removal of the silicon required a 10-μ porosity filter. The filtration rate was only 2 gal/(hr)(sq ft) at 20 in. mercury vacuum. Dispersion coalescence tests showed some minor surface activity, but in general the adsorptive and emulsification properties frequently associated with silica residues were not detected.

Dissolution of Dejacketed Material

If fuel jackets can be removed mechanically or chemically or the fuel sheared into pieces, dissolution of the irradiated core becomes a separate and possibly simpler feed preparation approach.

Studies at Hanford on dissolution of uranium-molybdenum alloys in nitric acid show that 3 per cent alloy may be dissolved to terminal uranium and nitric acid concentrations of 0.5*M* and 2*M*, respectively, without solids formation if the nitric acid is maintained below its boiling point, or if the initial nitric acid concentration is not over 6*M*. Dissolution in nitric acid–aluminum nitrate solutions could be performed without appreciable solids formation[8] if the terminal uranium concentration was held to less than 0.5*M*, the Al/F mole ratio to less than 0.5, and the F/Mo mole ratio to greater than 10 in the final solution.

It was found at Savannah River[9] that a 10 wt.% molybdenum–90 wt.% uranium alloy (Detroit-Edison fuel elements) dissolved readily in boiling nitric acid containing small quantities of fluoride ion. The effects of varying fluoride and nitric acid concentrations are shown in Fig. 4. At Hanford[2] a 9 wt.% molybdenum-uranium alloy was dissolved in nitric acid–hydrofluoric acid–aluminum nitrate–stainless-steel solution without formation of appreciable solids.

MTR plutonium-aluminum fuel elements dissolved in mercury-catalyzed nitric acid containing uranyl nitrate evolved hydrogen at a sufficiently low rate that explosive concentrations could reasonably be prevented by air dilution under plant operating conditions.[17]

Boiling 13*M* nitric acid–0.04*M* sodium fluoride appears to be a suitable dissolvent[18] for the 96 per cent thorium dioxide–4 per cent uranium dioxide fuel-element core material similar to

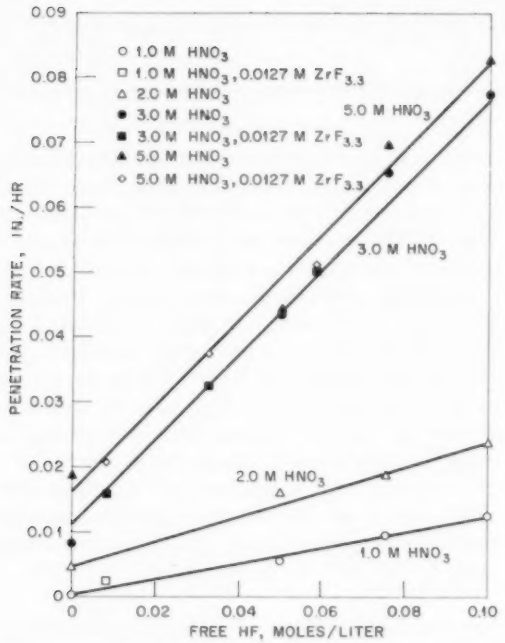

Figure 4—Dissolution of 90 wt.% uranium–10 wt.% molybdenum alloy.[9]

that to be used by Consolidated Edison. Dissolution of unirradiated ¼-in.-diameter pellets was 98 per cent complete in 5 hr, producing a final product solution of 8.6*M* nitric acid–1*M* $Th(NO_3)_4$–0.041*M* $UO_2(NO_3)_2$ at an over-all average dissolution rate of 3.4 mg/(sq cm)(min). Extrapolation of the rate data indicates that complete dissolution could be achieved in 6 to 7 hr. The total dissolution time was 1 to 2 hr for pellets that had been crushed to a powder. Sulfuric, nitric, and hydrofluoric acids and aqua regia were ineffective dissolution agents.

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Solvent Extraction

Purex Process Improvements, Modifications, and New Developments

Redox and Purex are the principal solvent-extraction processes currently in use. Work continues in an effort to improve them and to adapt them to a variety of separations problems.

Various head-end treatments, discussed in these Reviews under the heading "Preparation for Fuel Processing," are being developed to accommodate power reactor fuels for Purex and Redox processing. Inactive feed solutions prepared via the Darex head-end treatment for stainless-clad fuels (aqua regia dissolution) have been successfully processed for uranium recovery under Purex conditions. By using an extractant of 2.5 per cent tributyl phosphate (TBP) in kerosene and a total nitrate salting strength of about 6*M*, uranium was extracted with a processing loss of only 0.001 per cent.[1] A feed solution prepared from unirradiated Detroit-Edison reactor fuel elements (10 per cent molybdenum-uranium alloy clad in zirconium) by dissolution in a mixture of 3.0*M* nitric acid and 0.05*M* hydrofluoric acid was processed under Purex conditions using 10 per cent tributyl phosphate in ultrasene. Uranium was extracted with low losses, but further process development is necessary if it is desired to reduce high plutonium losses associated with the complexing action of fluoride ion.[2]

Purex modifications for neptunium recovery have been under development for some time. For extraction of neptunium by either methyl isobutyl ketone or tributyl phosphate, the +4 or +6 valence states are required; Np(V) is unextractable. Dichromate, 0.01*M* to 0.08*M*, was added to the Purex first-cycle extraction contactor scrub solution. Near quantitative recovery of neptunium in the organic product steam was realized with reasonably low plutonium losses. However, fission-product decontamination was adversely affected.[3]

In Purex processing, the actual extractant has been identified as a tributyl phosphate–nitric acid complex.[4] The extractability of uranium from sulfate solutions with diluted TBP is poor;[5] however, the addition of nitrate ion can provide a favorable extraction environment. Uranium was recovered from solutions containing as much as 2.5 moles of sulfate per mole of uranium by the addition of nitrate ion as aluminum nitrate and nitric acid. By using 15 moles of nitrate per mole of sulfate in the processing of uranyl sulfate from the Raleigh research reactor, uranium was extracted with losses of only 0.008 per cent. Satisfactory decontamination was realized, the gross beta decontamination being 1×10^5 and the gross gamma, 2.4×10^3.

Process Applications of Organophosphorus and Organonitrogen Extractants

The development of process applications for the organophosphorus and organonitrogen extractants appears certain to have considerable effect on the future of solvent-extraction fuel processing. The unique feature of these extractants, discussed in detail in an earlier Review,[6] is that they may be considered as liquid ion-exchange agents. Hence they are amenable to a wide variety of processing schemes and separations problems.

A solution of tri-*n*-octylphosphine oxide (TOPO) in cyclohexane diluent was demonstrated as an excellent extractant for thorium from nitrate and chloride solutions but not from sulfate and phosphate solutions.[7] The thorium complex formed was postulated as

$$ThCl_4 \cdot HCl \cdot 3(TOPO)$$

$$Th(NO_3)_4 \cdot HNO_3 \cdot 3(TOPO)$$

As shown in Fig. 5 the extraction coefficients are appreciable being 2000 in 1*M* nitric acid and 200 in 7*M* hydrochloric acid. TOPO extraction of thorium from phosphate and sulfate solutions was poor with extraction coefficients of the or-

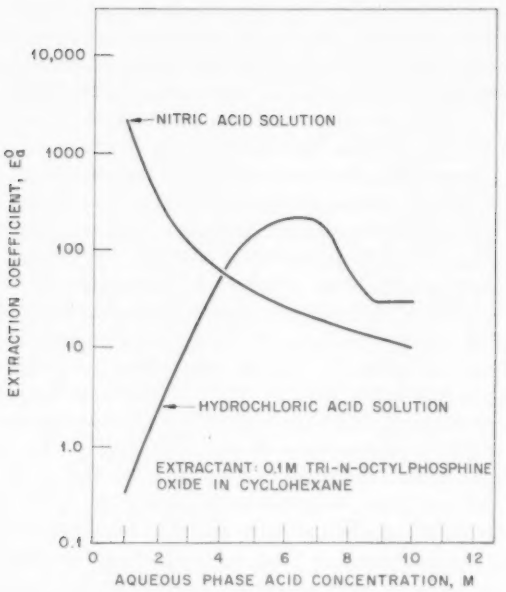

Figure 5—Effect of acid concentration of tri-n-octylphosphine oxide extraction of thorium.[7]

der of 0.3 reported for sulfate solutions. Upon the addition of nitrate or chloride ion, however, the extractability of thorium was markedly improved such that in a single batch equilibration 99 per cent of the thorium was extracted from an aqueous sulfate solution.

Fundamental Solvent-extraction Studies

A thermodynamic interpretation of experimental data on the separate and combined distribution of nitric acid and uranyl nitrate between aqueous solution and tributyl phosphate in various diluents has been developed.[8] The assumption was made that a relatively stable solvate is formed as follows:

$$UO_2^{+2} + 2NO_3^- + 2TBP \rightleftharpoons UO_2(NO_3)_2 \cdot 2TBP \qquad (1)$$

The nonideality of solutions of uranyl nitrate in TBP was attributed to solvate formation effecting depressed activity of uranyl nitrate. By relating the uranyl nitrate distribution coefficients to the equilibrium coefficient for Eq. 1, relations were developed to calculate the organic phase concentration of uranyl nitrate in equilibrium with a given concentration in the aqueous phase.

From experimental data for 20 per cent TBP, distribution curves in excellent agreement with experimental data were calculated for 10 and 40 per cent TBP. Extrapolation over a larger range of dilutions, however, led to progressively greater deviations.

The study of the distribution of nitric acid was based on the assumption of the formation of a monosolvate. By combining the equations for nitric acid with those for uranyl nitrate, an estimate was made of the effect of nitric acid on the distribution of uranyl nitrate. Comparison of the nitric acid and uranyl nitrate systems showed that the degree of binding by TBP was a function of TBP dilution in the case of uranyl nitrate but not in the case of nitric acid.

Degradation of Process Solvents

Process solvents undergo degradation as a result of chemical and radiation damage. Increasingly more severe chemical and radiation environments will be encountered in the processing of nonproduction reactor fuels. Therefore considerable effort is being devoted to assessing the stability of current process solvents, to the evaluation of alternate extractants, and to the removal of degradation products from used solvent.

The objectionable degradation products are those which form insoluble compounds, solvent-soluble fission-product complexes, unstrippable uranium or plutonium complexes, and surface-active agents. No entirely satisfactory test of solvent quality has been developed. However, two tests are available which provide fairly rapid semiquantitative techniques for assessing the degree of objectionable solvent degradation. One is the "Z" test which is based on the retention of tracer zirconium by degraded solvent. The other is an emulsification test where solvent is mixed under standardized conditions with the appropriate aqueous solution and the emulsion settling time noted.

Conventional recovery procedures for used solvent, which involve washing with aqueous caustic solutions, are not adequate for severely degraded solvent. Tests showed that even an expensive vacuum distillation treatment was of no value in the recovery of degraded TBP-Amsco solvent.[9]

Kerosene diluents employed in the Purex process undergo chemical degradation by reaction with nitric and nitrous acids. Ultrasene, the

diluent in the Savannah River Purex plant, is more susceptible to chemical degradation than Amsco. A number of alternate diluents were tested under standardized conditions. *N*-dodecane specially treated to remove olefins proved to be the most stable as indicated in Table IV-1 by the lower "Z" numbers.[10]

Table IV-1 STABILITY OF PUREX DILUENTS EXPOSED TO CHEMICAL DEGRADATION[10]

Diluent	"Z" Number[12] 40°C	70°C
Ultrasene	800	375
Amsco 125-82	120	85
N-dodecane (olefin free)	40	110
C_{12} n-paraffin (commercial)	50	90

The principal Purex solvent degradation products are mono and dibutyl phosphate which strongly complex uranium and plutonium in the organic phase. Butanol and butyraldehyde, also produced, were reported as having no appreciable effect on solvent performance. Purex solvent, with 20 per cent TBP, irradiated to 10 watt-hr/liter was first contacted with a plutonium feed solution and then an aqueous stripping solution. A plutonium precipitate was observed on stripping. The retention of unstrippable plutonium in degraded Purex solvent was as high as 10 μg/ml after solvent irradiation to a modest 1 watt-hr/liter.[11]

In the Redox process, degradation of methyl isobutyl ketone is brought about by strong nitric acid solutions and by irradiation. As alternate extractants, the straight chain polyethers are the most attractive with extractive capacities approximating that of hexone. Exposure of dimethoxyl hexane to 5*M* nitric acid initially 0.01*M* nitrate under conditions which result in vigorous reaction with methyl isobutyl ketone (30 min at 80°C) resulted in a very slight discoloration. Successful demonstration of a satisfactory alternate extractant will permit the Redox first cycle to be operated with acidic feeds such as are produced in the dissolution of many power reactor fuels.[3]

A possible alternate extractant, diethyl carbonate (DEC), was irradiated to 392 watt-hr/liter and contacted with various aqueous process solutions. On contact with aqueous 0.01*M* nitric acid stripping solution, no evidence of the formation of unstrippable uranium complexes was noted. Emulsification tests showed that the settling characteristics of the solvent were not adversely affected as is the case with tributyl phosphate. However, analyses of irradiated DEC showed appreciable decomposition to the extent of 5.5 molecules per 100 ev of energy absorbed.[13]

In general, the more recently developed organonitrogen and organophosphorus compounds have demonstrated more resistance to irradiation than tributyl phosphate. Studies of dibutylphenylphosphonate (DBPP) irradiated from 100 to 1500 watt-hr/liter showed acid formation of 0.36 molecules per 100 ev of energy absorbed, some three to four times lower than the corresponding acid yield of TBP.[13] Solutions of trilaurylamine (TLA) and *n*-benzylheptadecylamine (NBHA) diluted with 95 per cent Amsco−5 per cent tridecanol were irradiated from 100 to 400 watt-hr/liter. Emulsification tests for solvent degradation showed little effect of irradiation on 0.1*M* solutions of TLA or NBHA but revealed pronounced emulsification tendencies for 0.5*M* of TLA.[14] DBPP in Amsco-tetralin, after irradiation to 200 watt-hr/liter, when tested for emulsification tendencies actually demonstrated a *decrease* in settling time in contact with an aqueous solution of calcium hydroxide.[14] Solutions of 0.1*M* TLA and NBHA in Amsco, irradiated to 100 to 200 watt-hr/liter and contacted with solutions of uranyl nitrate and nitric acid, settled nearly as rapidly as the unirradiated control. The settling time of 0.5*M* TLA increased by a factor of 12. Settling times of solutions of DBPP in Amsco or Amsco-tetralin (150 to 250 g DBPP per liter) irradiated to 200 watt-hr/liter were greater by factors of 2 to 3 than unirradiated controls.[1] Solutions of TLA diluted with Amsco or xylene were irradiated to 52 watt-hr/liter and evaluated under process conditions. Results showed that degradation of the diluent caused inferior zirconium-niobium decontamination and that Amsco was inferior to xylene. Decontamination factors on irradiation dropped from 2.6×10^4 to 3.4×10^3 with xylene and from 2.2×10^4 to 630 with Amsco.[15]

Nuclear Safety and Criticality

A handy summary of much of the published information on nuclear safety has been published.[16] Data are presented on Pu^{239}, U^{235}, and U^{233} as metals, compounds, and solutions. Mass limits for various fissionable materials in several basic configurations are presented con-

servatively with factors of safety of about 2. The effect of a thick water reflector, a thin water reflector (for example a jacketed vessel), and a minimal reflector (usually the walls of the container) are considered.

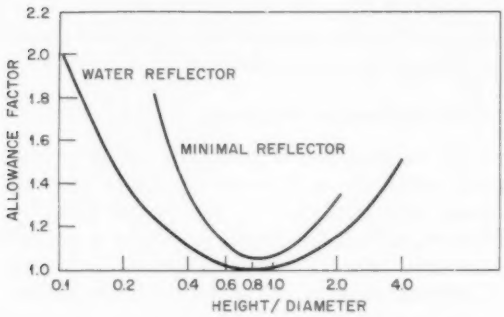

Figure 6—Allowance factors for cylinders.[16]

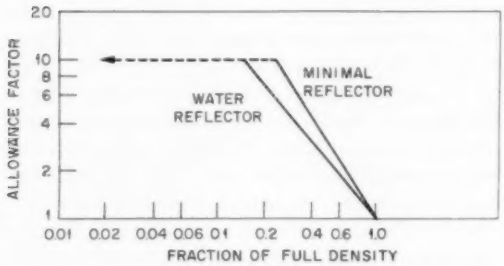

Figure 7—Allowance factors for reduced density U^{235}, Pu^{239}, or U^{233} (reference 16).

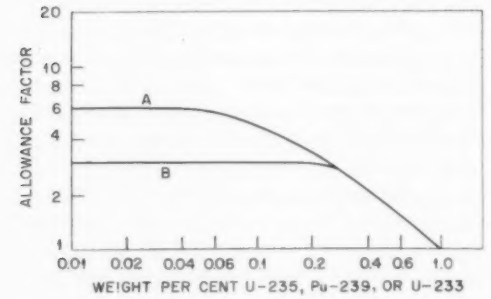

Figure 8—Allowance factors for compounds and alloys.[16] A, alloys containing elements of atomic number $11 \leq Z \leq 83$. B, compounds containing C, N, O, F, or elements $11 \leq Z \leq 83$.

Especially useful are a series of empirically formulated correlations of allowance factors. These factors facilitate the extrapolation of experimentally determined criticality data. Figure 6 provides allowance factors for cylinders of undiluted fissionable material. The minimum critical mass is indicated for a cylinder with height-to-diameter ratio of about 0.8. The critical mass for a cylinder of other relative dimensions would be greater by the factor indicated. Figure 7 provides allowance factors for reduced density. A typical example of reduced density would be metal turnings from machining operations. Figure 8 provides data for determination of safe mass limits for compounds and alloys of various compositions. The shape allowance factor correlations may be used separately or in combination. When used with the conservative mass limits, they permit the rapid estimation of safe specifications for a wide variety of physical and chemical conditions. For the specific case of plutonium-aluminum alloys some calculated values are available.[17]

Precipitation Processes

The precipitation of plutonium compounds has been discussed in recent literature from the viewpoints of both intentional and unintentional precipitations in fuel processing and product recovery operations.

Elemental plutonium is prepared at Los Alamos Scientific Laboratory from plutonium nitrate solution by a process that starts with peroxide precipitation to purify and concentrate the plutonium.[4] Although the yield of plutonium is normally excellent, there are factors such as acidity, oxidation state of the plutonium in the feed solution, and specific impurities that cause peroxide decomposition which must be controlled if a good yield is to be realized.[18]

The effect of acidity can be minimized by the use of a large excess of hydrogen peroxide. Routine plant precipitations (300-g batches) from an acidity of 2.5*M* result in solubility losses of less than 0.1 per cent. The presence of hexavalent plutonium can have a pronounced effect on yield. Reduction of Pu(VI) to Pu(IV) by hydrogen peroxide at ambient temperatures is slow. When feed solutions contain a high proportion of Pu(VI) and Pu(V), it is frequently more convenient to reduce them on a batch basis before introduction into the process. The presence of large amounts of certain impurities such as iron may reduce yield because ferric ion in the presence of peroxide can oxidize Pu(IV). More-

over, the decomposition of peroxide by iron, copper, or manganese can result in excessive oxygen liberation and heat evolution, which interferes with control of the precipitation. In such cases, the plutonium may be purified by batch precipitation as the oxalate prior to introduction into the plant process.

Good purification of plutonium from most impurities is obtained by peroxide precipitation. In tests of 26 impurity elements in all periodic groups except Group V, good purification was effected from all except zirconium and the actinide impurities, uranium and thorium.

The incipient precipitation of colloidal Pu(IV) hydroxide in processing solutions of low acidity may result in the formation of critically unsafe deposits and plugging of transfer lines. The presence of the colloid also causes foaming during concentration by evaporation and emulsification in solvent-extraction operations. The conditions necessary to avoid hydrolytic polymerization of quadrivalent plutonium have been studied.[19]

The polymerizing plutonium hydroxide is formed by the hydrolysis of plutonium nitrate. The solubility of the polymer increases with nitric acid concentration. The rate of particle formation will therefore be high if acidity is low, and particles of colloidal dimensions will be formed. Higher acid concentrations favor the formation of a precipitate rather than a colloid. The more difficult solubility of precipitates formed at higher temperatures suggests that the polymer may be partly an oxide or suboxide.

The rapid rate of polymer formation and the slow rate of depolymerization make possible the existence of the polymer in solutions subjected only to transient unstable conditions. The polymer may form in overheated pumps or in places where steam or water leaks might cause dilution. It may be deposited at the place of formation or carried by the solution as a colloid.

To avoid this serious problem in handling low acid Pu(IV) solutions, it is suggested that conditions leading to possible localized high temperatures or water dilution be avoided. Temperatures employed in concentration by evaporation must not exceed the precipitation temperature for the solution. Plutonium(IV) solutions should be diluted with acid; never purposely with water. Depolymerization should be effected at the highest practical acidity and temperature.

Ion-exchange Processes

Ion-exchange processes have been applied to the purification and recovery of plutonium, uranium, and neptunium; fundamental studies on the behavior of metal ions in solution are reported; the removal of cesium from alkaline solutions is discussed, and methods of fission-product separation from uranium and plutonium are reported.

Anion-exchange Processes

The purification of plutonium by absorption from nitric acid solution by anion-exchange resins was described at Geneva by Ryan and Wheelright.[20] Anion exchange offers a marked advantage over cation exchange for plutonium processing because of the ease of decontaminating the plutonium from all normally encountered impurities. Anion exchange had been applied as a primary method for the separation of plutonium from irradiated uranium, but processing rates and product concentrations were low. By operating at elevated temperature (50 to 60°C) and by proper choice of anion-exchange resins, throughputs may be increased considerably, product concentration increased, decontamination improved, and the use of reagents other than nitric acid eliminated. Absorption and elution flow rates as high as 80 mg plutonium/(min)(sq cm), decontamination factors of greater than 5×10^3 for fission products and greater than 5×10^4 for uranium and other metallic impurities, and product concentrations of above 50 g plutonium/liter are readily attainable in a single anion-exchange cycle under proper operating conditions. The method is both chemically and mechanically simple.

Because of the high fission-product decontamination potential when a wash cycle is inserted between the absorption and elution cycles, anion exchange can be coupled to a one-cycle solvent-extraction process to give essentially complete recovery and decontamination of plutonium. A flow sheet showing the manner in which an anion-exchange process can be coupled to a simplified Purex partition cycle is shown in Fig. 9. Fission-product decontamination factors shown on this flow sheet are those which were obtained in a laboratory test of this operation in which the solvent-extraction cycle was simulated in bench-scale mixer-settlers with synthetic feed. Comparison of the flow sheet shown in Fig. 9 with typical Purex flow sheets shows

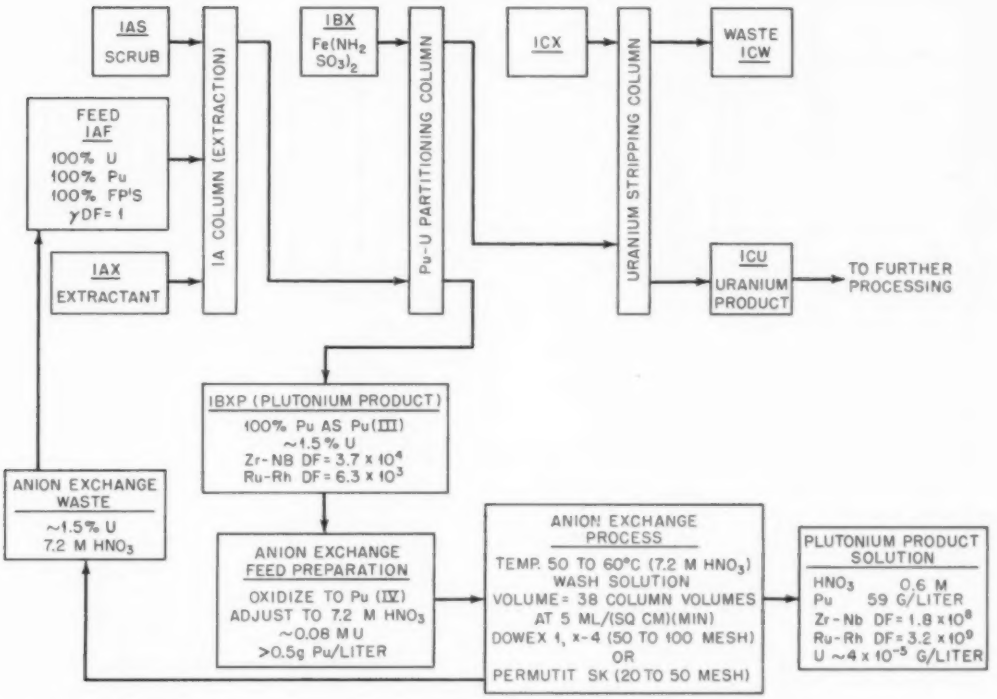

Figure 9—Combined solvent extraction–anion-exchange flow sheet for plutonium recovery and decontamination.[20]

that a single cycle of anion exchange can replace the second plutonium cycle and can partially replace a thermal evaporation step when one is used to concentrate the plutonium products. A series of static bed columns or a continuous contactor can be used. Permutit SK (20 to 50 mesh) resin would be preferred in a Higgins type moving bed contactor. The column dimensions and operating conditions will depend upon the processing rate desired, but loading and elution zones of at least 6 ft should be provided if feed rates of 80 mg plutonium/(sq cm)(min) are to be approached.

Anion-exchange processes are expected to find considerable application in the processing of plutonium reactor fuels. In particular, the anion-exchange process is being studied as a potential processing method for plutonium recycle reactor fuels, which could be installed in a low-cost close-coupled processing plant located at the reactor site. One of the several possible ways in which anion exchange could be applied to the processing of fuel from such a reactor is illustrated by the simplified flow sheet[20] of Fig. 10.

Purification of plutonium nitrate solutions by anion exchange is being studied at Hanford.[21] Data indicate that Purex first-cycle plutonium product solution can be effectively decontaminated by one cycle of anion exchange using Permutit SK. Addition of aluminum nitrate to the fluoride containing wash solution cuts down the plutonium loss without sacrificing zirconium removal. The use of a wash solution containing 7.2*M* nitric acid, 0.056*M* hydrofluoric acid, and 0.056*M* aluminum nitrate interposed between two nitric acid washes gave a satisfactory zirconium-niobium decontamination factor.

The feasibility of producing adequately decontaminated plutonium product by one cycle of anion exchange applied to Purex 1BP was again demonstrated.[3] The feed for this run was prepared by adjusting fresh Purex plant 1BP to 7.2*M* nitric acid by addition of concentrated nitric acid. This feed contained zirconium-niobium activity at a level higher than the feeds used in earlier work.

Data from three runs confirm the beneficial effect of addition of fluoride in the loading and

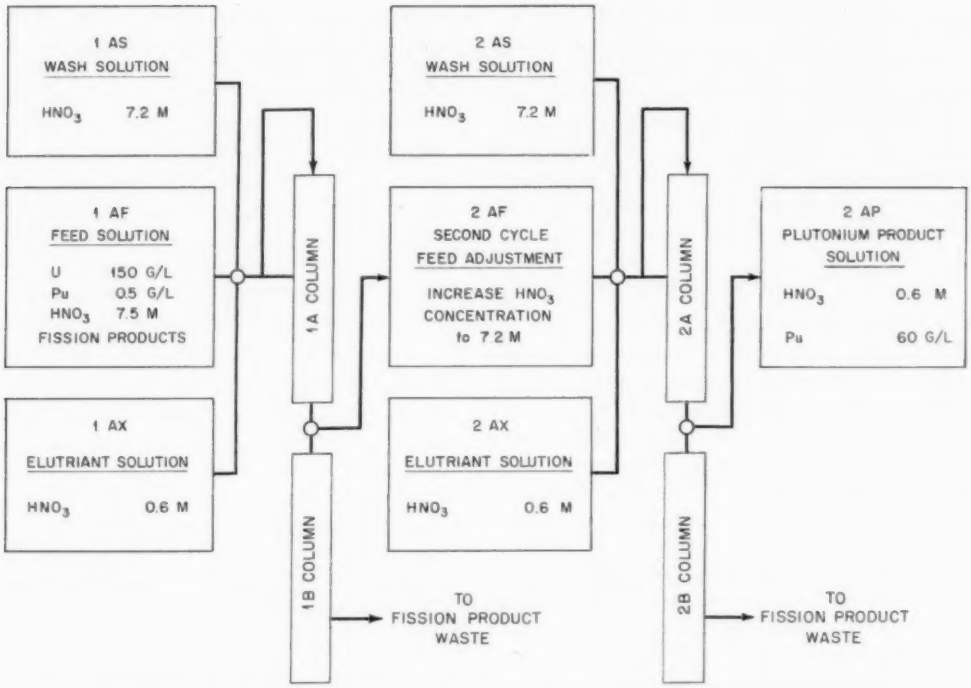

Figure 10 — A two-cycle anion-exchange flow sheet for processing plutonium reactor fuels.[20]

wash cycles in improving decontamination of plutonium from those fission products present[15] in Purex 1BP. Of particular interest is a run in which the feed was made up to 6.1*M* nitric acid, 0.06*M* hydrofluoric acid, and 0.3*M* aluminum nitrate, in place of 7.2*M* nitric acid in the usual case. Plutonium breakthrough occurred somewhat earlier in this run.

Impurity concentrations of aluminum, calcium, chromium, iron, magnesium, manganese, nickel, and zinc in plutonium were determined by an anion-exchange spectrographic method.[22] Plutonium was separated by adsorption of the nitrate complex on Dowex-1. The impurities were determined in the effluent by d-c arc excitation with cobalt as the internal standard. Concentrations as low as 2 ppm impurity in plutonium in 50-mg samples were determined with a precision of ±12 per cent.

The Excer process[23] used for the recovery of uranium from a chloride system by anion exchange is shown schematically in Fig. 11. Ore concentrate is dissolved in hydrochloric acid, purified by anion exchange, electrolytically reduced to uranium tetrachloride, and then precipitated as hydrated uranium tetrafluoride by the addition of hydrofluoric acid. The hydrated uranium tetrafluoride is filtered, dried, pelletized, granulated, and then dehydrated in a fluidized-bed dehydrator at 450°C. In the anion-exchange purification step decontamination factors of greater than 10^3 were realized for all impurities except trivalent iron, pentavalent vanadium, and molybdenum. These three impurities were removed in the uranium tetrafluoride precipitation step with a decontamination factor of 10^3. The final dehydrated uranium tetrafluoride was contaminated primarily with stainless-steel products which probably were introduced in the dehydration step.

Optimum conditions for uranium recovery from a stainless-steel decladding solution were obtained in the 0.5*M* SO_4^{-2} range using Dowex-1 anion resin.[24] The uranium product was eluted from the resin with nitric acid and was contaminated with less than 0.01 per cent of the stainless-steel components. Distribution coefficients were determined for uranium between Duolite C-65 cation resin and Dowex-1 anion resin and sulfuric acid in the 0.45*M* to 0.56*M*

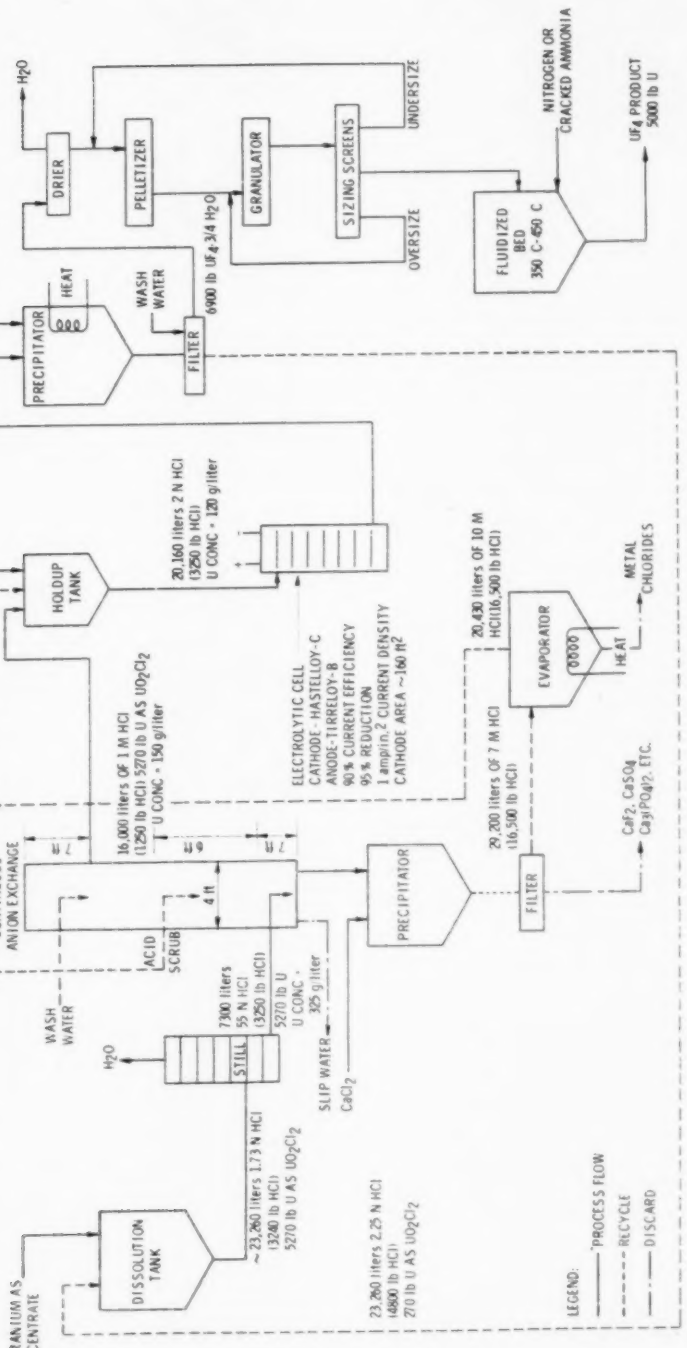

Figure 11 — Treatment of ore concentrate by the Excer process, chloride system, for recovery of uranium.[23]

range. The distribution coefficients varied from 30 to 77. Duolite C-65 resin showed some possibility for uranium recovery, but Dowex-1 in the 0.5*M* SO_4^{-2} range was the most promising, according to the distribution coefficients.

Neptunium can also be isolated by anion exchange from concentrated nitric acid solutions. Work at Hanford[3,15,21] on absorption of neptunium onto 20- to 50-mesh Permutit showed that neptunium recovery is marginal under conditions that correspond to a high uranium recycle and high flow rates.

Cation-exchange Processes

A continuous cation-exchange process is being studied for the removal and recovery of high-purity cesium from alkaline waste.[25] Cesium is selectively sorbed on a phenolic methylene sulfonic resin, Duolite C-3, along with strontium, the rare earths, and other cationic fission products. At feed rates up to 2000 gal/(sq ft)(hr), tracer activities in a synthetic alkaline waste solution were reduced to background levels of 0 to 50 cpm/ml, corresponding to decontamination factors of $>10^4$ for cesium and $>10^3$ for strontium and the rare earths. Cesium was removed from the contactor by selective elution with hydrochloric acid to produce a product containing about 1 per cent sodium along with tracer quantities of strontium and the rare earths.

Use of ion-exchange methods for a systematic fission-product separation was studied by Minami, Honda, and Sasaki.[26]

The separation of uranium and plutonium from zirconium, niobium, ruthenium, and cesium on a column of manganese dioxide has been investigated.[27] The adsorption of uranium, plutonium, zirconium, niobium, ruthenium, strontium, yttrium, and cesium was examined to provide a good separation of uranium and plutonium from the fission products mentioned. The UO_2^{+2} and PuO_2^{+2} were washed quantitatively from a column of manganese dioxide with 0.1*N* nitric acid. Under the same conditions, 99.2 per cent of Zr^{95}, Nb^{95}, Ru^{106}, and Cs^{137} was adsorbed.

Volatility Processes

Development has continued on various aspects of volatility processing, i.e., processes in which fluorination is used to convert uranium to volatile uranium hexafluoride and decontamination is subsequently effected by distillation or by absorption techniques. Information is included in this Review on interhalogen–uranium hexafluoride separations and fused-salt processing studies.

Interhalogen – Uranium Hexafluoride Separation

A low temperature fluoride volatility process using liquid bromine fluorides to dissolve and fluorinate uranium metal has been studied at BNL and ANL.[28] In this process, the product uranium hexafluoride is decontaminated and purified by fractional distillation. High decontamination factors have been demonstrated, but for some uses, very high chemical purity, particularly in regard to bromine, of uranium hexafluoride is also required.

Recently a packed-column separation of high-purity uranium hexafluoride was made from bromine pentafluoride which has a volatility closer to uranium hexafluoride than other bromine fluorides.[29] The column used in this study had a 1.75-in.-I.D. nickel fractionating section 16 ft long packed with Heli-Pak 3019. By means of a vapor circulation system, the column was operated as a steady-state stripping section at 45 psia and approximately 90°C. Because lower fluorides of bromine were observed during previous column operation, a small amount of fluorine was bled through the packing. This served to prevent bromine pentafluoride degradation. The results of vapor samples taken during the run are shown in Fig. 12. HTU values of approximately 10 in. were calculated for this separation, assuming Raoult's law and a relative volatility of 1.4 for bromine pentafluoride–uranium hexafluoride. This HTU value is about four times that obtained for a hydrocarbon test system but is not inconsistent with data from previous separations of interhalogen mixtures. Vapor-liquid and liquid-solid equilibria for systems containing uranium hexafluoride, chlorine trifluoride, and hydrogen fluoride were presented at Geneva.[30] Systems containing hydrogen fluoride have low-boiling azeotropes.

In a recent publication on the liquid-vapor equilibrium for the system uranium hexafluoride–bromine pentafluoride, an azeotrope was reported by Ellis et al.[31] at about 0.1 mole fraction uranium hexafluoride. The results of a distillation of a bromine pentafluoride–uranium

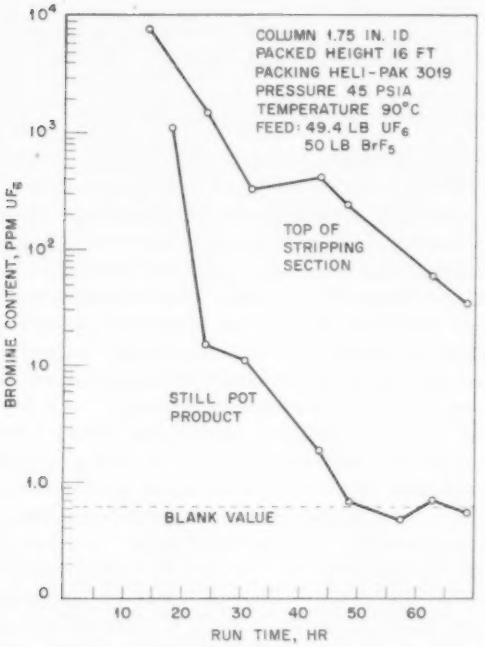

Figure 12—Separation of bromine pentafluoride–uranium hexafluoride mixture.[29]

hexafluoride mixture in a 1-in. packed column were also reported. The overhead vapor composition was observed to change with pressure, and these variations were attributed to a shift in the azeotropic composition. However, critical examination of these data of Ellis raises serious doubts as to whether an azeotrope exists in this system.[32] The following points may be cited: (1) the vapor pressures determined for bromine pentafluoride are high compared to data by Long;[33] (2) no precautions against reduction of bromine pentafluoride were mentioned; (3) column separations could be limited by the number of stages rather than by an azeotrope; (4) recent work (in progress)[32] on this system failed to confirm the azeotrope.

Fused-salt Processing

Additional fused-salt processing studies have been carried out at the ORNL pilot plant. Fused-salt reactor fuel (containing uranium) was spiked with amounts of plutonium corresponding to those expected from 25 per cent burn-up of highly enriched fuel. Ninety-eight per cent of the plutonium remained in the salt; the uranium hexafluoride product contained 3.4 parts per billion plutonium or less.[34] Therefore plutonium contamination of the uranium hexafluoride is considered not to be a problem.

In a study of the valence changes during the fluorination of sodium fluoride–zirconium tetrafluoride salt containing 4 mole % uranium tetrafluoride, the fluorine consumption resulting from vessel corrosion reached a maximum at a U(VI) to U(IV) ratio of 1.7. Also it was reported that uranium was successfully recovered from molten potassium fluoride–zirconium tetrafluoride (40 to 60 mole %) by fluorination at 600°C.

Pyrometallurgical Processing

Pyrometallurgical processes are under development for the undelayed processing of fissile and fertile materials discharged from reactors. Because they offer promise of reduced processing costs, their development is an integral feature of the drive to achieve economic nuclear power.

Melt Refining

Melt refining* is the fuel purification process which is to be incorporated into a closed fuel cycle for the EBR-II (Second Experimental Breeder Reactor). The Fuel Cycle Facility for the EBR-II complex is now under design by ANL and its architect-engineer, the H. K. Ferguson Company, Cleveland, Ohio.[35] Drawings and specifications which will comprise a "bid package" are expected to be completed soon for submittal to interested and qualified contractors. The Laboratory and Service Building is already under construction (about one-third complete) by the Stewart Construction Company of Tucson, Arizona.

Meanwhile, work is continuing at Argonne on the design and testing of specialized equipment for remote operation, on testing and selection of materials for reliable service in high-radiation fields, and on further development of the melt-refining process and the fuel refabrication method.[35] Much of the equipment is being mocked-up for full-scale operation. Thirty, inactive, 10-kg runs have been made in a full-size melt-refining furnace. Yields of purified

*Irradiated fuel melted in a zirconia crucible and held molten for several hours allowing purification to occur through vaporization and crucible reactions.

material varied between 95 and 97 per cent. (Yields may not be quite as good with actual irradiated material but are expected to be above 90 per cent.) The entire initial fuel loading is to be prepared by using the same steps and types of equipment now planned for use in the Fuel Cycle Facility. This will serve for testing operating procedures and equipment, for the accumulation of data on alloy compositions and comparison of analytical methods, and for training of personnel.

Further information from laboratory studies is available on behavior of individual fission products. (It may be recalled that rare-earth and alkaline-earth fission products are removed through oxide formation, while others such as the noble gases, halogens, and cesium are removed by vaporization. Some noble elements, particularly molybdenum, ruthenium, rhodium, and palladium, are not removed.) An important mechanism of iodine removal, which has been shown to be virtually complete at process concentration levels, is reaction with crucible contaminants to produce volatile iodides of calcium, iron, and magnesium. About one-quarter of the iodine was evolved as molecular iodine. The data showed that about 70 per cent of the iodine diffused through the zirconia crucible walls whose total porosity was about 20 per cent.

No removal of zirconium from a plutonium-"fissium" alloy was realized by melt refining in either lime-stabilized zirconia or magnesia crucibles. A similar result was previously found for uranium-fissium. If desired, zirconium removal may be effected through carbide formation.

In connection with the removal of zirconium as the carbide, information has been obtained on the joint solubilities of zirconium and carbon in uranium at 1400°C. The concentrations measured for uranium and carbon provide a tentative liquidus line in the high uranium region in the ternary system: zirconium, carbon, and uranium. The values indicate it is possible to remove zirconium by carbide liquation to less than 0.01 wt.%. Preparations are nearly complete for investigating removal of zirconium by carbide liquation from plutonium-fissium alloys.

Further work on the Pyrometallurgical Refabrication Experiment (PRE), an engineering-scale operation for the remote processing and refabrication of irradiated uranium fuel from SRE type reactors, is being discontinued in accordance with an AEC directive.[36] This has resulted from the emphasis now being given to use of uranium dioxide fuels in these reactors.

Processing of Plutonium-rich Fuels

The Plutonium Recycle Project (Hanford) is concerned with the development of efficient chemical processing methods for preparation of plutonium and uranium alloys, recovery of plutonium from irradiated fuel, and the restoration of the plutonium content in depleted fuel material. The processes being worked on involve, in general, selective reductions and oxidations using metal-fused chloride systems. Recent information[3,15] is summarized below.

In the two-phase system, aluminum and a fused-salt mixture of aluminum and potassium chlorides, plutonium distributes preferentially into the salt phase while uranium distributes preferentially into the metal phase. Separations are not quantitative but could be made sufficient by a few stages of countercurrent operation. With a salt-to-metal ratio of 1.5 and a uranium-to-plutonium ratio of 100, 7.7 per cent of the plutonium and 92 per cent of the uranium were in the metal phase. This agrees with values previously measured with each metal alone. The behavior of plutonium was unaffected by uranium present to as high as 15 wt.% in the metal phase.

The effect of a modification of the salt composition was investigated by replacing potassium chloride with sodium chloride. This resulted in higher distribution of uranium into the metal phase. The use of cesium chloride had an opposite effect. Both findings are in accord with theoretical studies.

Some other elements distribute between the salt and metal phase as follows: thorium and cerium are found predominantly in the salt phase, whereas protactinium is found largely in the metal phase. Extraction coefficients are sensitive to potassium chloride–aluminum chloride ratios. For example, thorium distribution coefficients (salt-to-metal) are 10 to 100 times higher in the aluminum chloride-rich portion of the phase diagram than in the potassium chloride-rich portion.

It is planned to recover plutonium from the salt phase by reduction with magnesium or calcium, possibly in zinc solution. Inasmuch as cerium accompanies plutonium through the process, some experiments were performed to test the removal of spiked cerium activity from a

1.5 per cent plutonium-aluminum alloy by liquation in a magnesia crucible. After holding at 1300°C for 2 hr, no cerium activity was detectable in the alloy. The question of simultaneous plutonium loss is unresolved.

Plutonium was recovered from a plutonium-zinc alloy button produced by the reduction of plutonium chloride from a sodium chloride–potassium chloride system with magnesium-in-zinc at 800°C by heating *in vacuo* for 2 hr at 600°C. This reduced the zinc content to less than 1 ppm of plutonium by weight. The residual magnesium content was estimated to be between 0.1 and 1 per cent. It is thought that complete removal of magnesium would have been accomplished had a temperature in the neighborhood of 800°C been used.

Processing of Uranium Oxide Fuel

Work is in progress at Atomics International on the development of equipment and methods for processing and refabricating highly irradiated, short-cooled uranium dioxide[37] fuels. A cyclic oxidation-reduction procedure is being employed to pulverize the fuel and effect release or volatilization of xenon, krypton, iodine, cesium, and tellurium. Bench-scale experiments indicate removal of rare earths to be possible by treatment with hydrogen chloride gas.

The oxidation rate of uranium dioxide and "fissia" pellets was only slightly affected by a change[36] in the partial pressure of oxygen from 155 mm Hg to as low as 2 mm Hg. The oxidation was indicated to proceed in two stages: an initial stage in which the reaction rate is fairly linear and reproducible and during which a thin oxide shell is formed on the pellets, and a second stage which begins as this shell expands and begins to crack away from the pellet therby exposing fresh surface. The reaction rate in this second stage is also linear but some 10 to 20 times faster than that of the initial rate.

In large-scale work, the kinetics of oxidation and reduction of 5½ lb of fissia (uranium oxide plus fission element oxides) were studied using air and mixtures of oxygen with helium or argon. Better control of the oxidation at high temperatures appeared possible with the inert gas mixtures. Pellets of fissia were reformed, with densities of up to 90 per cent of theoretical being achieved.

Removal of uranium dioxide from enclosing metal capsules has also been effected by oxygen oxidation. Some irradiated uranium dioxide fuel was successfully removed from a Zircaloy cladding by this method. Five remotely operated experiments were successfully completed in which the uranium dioxide was removed in the operating temperature range of 480 to 620°C and a flow rate of 0.5 to 0.7 cu ft of oxygen per hour. Visual examination revealed complete removal of uranium dioxide from the can. This uranium dioxide was subsequently pulverized by the chemical pulverization process of oxidation at 375°C and hydrogenation at 650°C.

Liquid-metal Processes

Liquid-metal solution processes are emerging as one of the most promising types of pyrometallurgical processes. Such processes involve solution of nuclear fuel or blanket metals in a volatile metal solvent such as zinc, cadmium, or mercury. A variety of steps may then be employed to achieve the necessary separations; for example, crystallization of pure metals or intermetallics through cooling or addition of metal precipitants, extraction with immiscible metals or fused salts, selective oxidation and reduction, and distillation. Final recovery of the purified metal is effected by distillation of the metal solvent. Because of the wide variety of conditions and process steps possible, accommodation of a variety of fuels should be possible.

In the present stage of development, a considerable amount of fundamental information is being developed without specific processes in mind. This includes solubilities of metal solutes as a function of temperature and solution composition, coprecipitation phenomena, phase diagram studies, various thermodynamic data, dissolution rate studies, and corrosion information. Without relating to a process, presentation of the information developed would seem disconnected. It seems preferable, therefore, to indicate broad areas of work and a few references.

Considerable mention has been made in previous Reviews of zinc as a uranium solvent. Information on this solvent may be found in recent ANL Chemical Engineering Division quarterly reports, progress reports from the Ames Laboratory, and a Geneva paper by Feder and Teitel.[38] Perhaps the most interesting recent measurements are activity coefficients of various metal solutes.[35] Some are exceedingly low. Cerium, for example, has an activity coefficient of around 10^{-9} in zinc. This is manifested by the unex-

pectedly easy, but wholly explainable, reduction of cerium oxide by metal solutes such as uranium and magnesium, which have activity coefficients of around 10^{-2}.

At ANL a program has been started to obtain data for cadmium as a solvent metal in order to permit a comparison between zinc and cadmium for various contemplated pyrometallurgical separations.[35] Cadmium possesses the considerable advantages over zinc of being readily contained in ordinary low carbon steels and various 400 series stainless steels and of permitting operation at lower temperatures. The uranium solubility in cadmium (about 2 wt.%), while less than half that possible in zinc, is adequate for process purposes. Recovery of uranium from cadmium by crystallization is also less satisfactory than with zinc because of the presence of a eutectic at a uranium concentration of about 0.05 per cent. It has been recently found, however, that this can be overcome by the addition of a small amount of zinc (~10 wt.%). The corrosion characteristics of this system at the moderate temperatures involved have not yet been ascertained.

Another important piece of information is that, as in the zinc system, plutonium coprecipitates well with the uranium-cadmium intermetallic (UCd_{11}). A uranium-plutonium separation may be effected by the addition of sufficient magnesium to decompose the intermetallic. This precipitates uranium while plutonium remains in solution. On the basis of the foregoing, a number of blanket processes may be devised to effect plutonium separation and recovery.

The phase equilibria of the thorium-mercury system have been studied[39] over the composition range 0 to 100 per cent and temperatures up to 1000°C. The solubility of thorium, however, as determined by an electrical resistivity method, is orders of magnitude higher than that reported by Oak Ridge workers[40] using a chemical procedure. A similar situation existed in the uranium-mercury system and seems resolved in favor of the chemical procedure. The resistivity method is apparently subject to error for unknown reasons. In the presence of a small amount of uranium (0.005 per cent), the thorium solubility in mercury was reported by the ORNL workers to be 0.0018 and 0.0282 per cent at 50 and 356°C, respectively. The uranium appeared to coprecipitate with the thorium.

The distribution of plutonium between uranium and some immiscible metals was reported by Ames[41] (Table IV-2). The high coefficient with silver is such that a single, equal-weight extraction will remove over 95 per cent of the plutonium. Much less plutonium is extracted by lanthanum and silver, so they probably have little application in separations work. Although the distribution coefficient is less favorable with magnesium than with silver, the higher volatility of magnesium makes possible easier removal from the plutonium by vaporization.

Table IV-2 DISTRIBUTION OF PLUTONIUM BETWEEN MOLTEN URANIUM AND SOME IMMISCIBLE METALS[41]

(Temp., 1225°C; Time, 20 min)

Element	Distribution coefficient (weight basis)
Silver	20 to 40
Lanthanum	0.64 to 0.90
Cerium	0.85
Magnesium*	2

* Not included in Ames work; data provided for sake of completeness.

Removal of noble fission products from a uranium-bismuth alloy by drossing with zinc has been reported (by the American Smelting and Refining Co.[42] doing contract work for Brookhaven National Laboratory). On a 40-lb scale and at 300°C, noble metal concentrations were reduced tenfold or more by the addition of 0.5 per cent zinc. The intermetallic zinc–noble metal drosses concentrated at the top of the melt. The uranium concentration was unaffected.

Use of a liquid-metal process requires development of engineering-scale equipment and techniques. Operations which will need to be effected are phase separation, liquid metal or fused-salt extraction, distillation and rectification of liquid-metal systems, molten-metal transfer, and various other materials transfer operations. Reasonably good separation of zinc mother liquor from precipitated U_2Zn_{17} crystals has been effected by siphoning off the mother liquor. Satisfactory separations can be made with the dip tube extending into the crystal bed because of the "log jam" or "wet sand" character of the crystal bed.[35]

Equipment has been constructed at Ames, Iowa, and at Argonne for studying separation of metals by vacuum distillation and for retorting intermetallic concentrates for recovery of uranium. Development of continuous multistage ap-

paratus for molten extractions is in progress at Ames.[43]

An 18-8 stainless-steel thermal convection loop which includes two flanged joints and a cold trap has been in operation at Ames for 3600 hr circulating a lead-bismuth eutectic mixture with hot leg and cold leg temperatures being gradually increased to 560 and 410°C, respectively.[43] Corrosion product concentrations have been low (100 ppm or less). Because of grain growth leading to subsequent cracking, attempts to fabricate an yttrium loop for circulating a uranium–5 wt.% chromium eutectic system have thus far been unsuccessful.

Extended tests (500 to 2000 hr) without failure have been reported[43,44] on the following types of flanged joints: (1) tongue and groove without gasket, (2) a low carbon steel ring gasket between flat stainless-steel flange faces, and (3) a 20-mil tantalum gasket between serrated stainless-steel faces. The tests were carried out with the lead-bismuth eutectic at pressures up to 50 psig and temperatures up to 500°C.

Miscellaneous

A new reference work,[45] Report BMI-1300, "Constitution of Uranium and Thorium Alloys," has been issued which supersedes a previous report, BMI-1000, "Compilation of U.S. and U.K. Uranium and Thorium Diagrams." Available information on both binary and ternary systems is given.

Homogeneous Reactor Processing

The homogeneous reactor concept is being studied at several sites: the aqueous homogeneous reactor at ORNL, the Liquid Metal Fuel Reactor (LMFR) at BNL, and the molten plutonium reactor at LASL. One of the advantages of the homogeneous reactor concept is the ability to remove a side stream from the fluid fuel for chemical processing purposes. With continuous side stream removal, the decontamination requirements of a chemical process need not be high. Data are presented in this Review only on the aqueous homogeneous reactor work.

A paper prepared for the Geneva Conference on the HRT-2 contains a section on the fuel processing plant including schematic diagrams and photographs.[46] A summary for the HRT chemical plant run number 16 was recently released.[47] Total operating time for the run was nearly 800 hr in which an accumulated power generation of 1235 Mw-hr was achieved. From nickel concentrations in the fuel, it was possible to calculate an average reactor corrosion rate of 1 mil/year. This corresponds to the production of more than 1000 g of stainless-steel corrosion product in the core and 1170 g in the blanket. The chemical plant hydroclones removed a total of 310 g. The fission-product activity distribution during the run is shown in Table IV-3. The discrepancy between the activity accounted for and that which would be expected from the reactor power history is probably attributable to the adsorption of these activities on the interior surfaces of the reactor system.

Run 17 of the HRT has also been completed.[34,48] Total operating time was 1074 hr for a total power production of 2526 Mw-hr (mostly at 3.5 and 1.8 Mw). The corrosion product solids accumulated in the hydroclone during the run analyzed 47 to 49 per cent zirconium, 19 to 23 per cent iron, 4 per cent chromium, and 1 per cent titanium. No fission-product data were reported. The initial fuel charge to the reactor system was reported to be decontaminated by solvent extraction.[13] Gadolinium was used as a soluble poison for criticality control during the processing operations.

Investigations are being made to determine the cause of the rare gas breakthrough during the start-up of one of the runs.[34,40,48] It has been postulated that part of the charcoal bed ignited resulting in combustion gases of carbon dioxide and carbon monoxide which in turn affected the efficiency of the adsorption of Kr^{85}. High carbon dioxide contents in the oxygen sweep gas reduce the dynamic adsorption coefficient. The ratio of carbon dioxide to carbon monoxide produced by combustion increases as the linear velocity of oxygen decreases or, in effect, as the reaction temperature decreases. These observations were found to conform with the observed abnormal behavior of the HRT charcoal bed.

In order to monitor adequately the performance of a hydroclone in the reactor system, it is desirable to dissolve completely the accumulated solid residues. A topical report has appeared[49] describing procedures which are adequate for this purpose.

Several British reports have been published relating to the chemical processing of aqueous homogeneous reactor fuel.[50-52] Methods are outlined[52] for calculating equilibrium fission-product levels for various power levels of a re-

Table IV-3 FISSION-PRODUCT ACTIVITY DISTRIBUTION[47]

(HRT Chemical Plant Run 16)

	Ru^{103}		Zr^{95}		Sr^{89}		I^{131}		Cs^{137}	
Run No.	16–2*	16–3*	16–2	16–3	16–2	16–3	16–2	16–3	16–2	16–3
Activity in chemical plant, curies	47	62	53	103	20	129	2.7	47	0.4	1.5
Activity in reactor, curies	12	31	21	96	4.2×10^3	2.0×10^4	46	1.9×10^3	67	199
Total accounted for, curies	59	93	74	199	4.2×10^3	2.0×10^4	49	1.9×10^3	68	200
Total expected from reactor power history	8.3×10^3	3.4×10^4	1.0×10^4	4.0×10^4	8.6×10^3	3.3×10^4	1.5×10^4	7.3×10^4	68	230
Per cent accounted for	0.7	0.3	0.7	0.5	49	61	0.3	2.6	100	87

* Second portion of run is identified as 16–2 and third part of run as 16–3; each represents several hundred hours of operation.

actor and for various types of processing. The latter include methods for gas removal, solvent extraction, precipitate removal, and plating out. Calculations are shown[51] for determining what such an equilibrium concentration might be for a typical core solution. Assumptions for this calculation include a 400-Mw reactor, solid separations at a rate of 20 liters/min (two core plus core-circuit volumes per day), and solution treatment at a rate sufficient to keep the nickel concentration below 0.02*M* (110 liters/day; core plus core-circuit volume is 14,600 liters). The resulting calculations include the radiolytic gases, corrosion products, corrosion and fission-product zirconium, and fission products.

Corrosion

Many of the chemical processes being devised for the purification and recovery of fissionable materials involve unusually corrosive chemicals. Corrosion programs necessarily follow. In this section an attempt will be made to cover progress on programs that have been set up to cover specific corrosion problems in a systematic manner.

Solvent Extraction

Newer reactors, both built and contemplated, often use fuel that cannot be processed directly in existing solvent-extraction plants. Efforts are being made at several sites to develop head-end treatments for such fuels so that resulting solutions can be processed in existing plants (references 3, 9, 13, 21, and 53). The Consolidated Edison reactor at Indian Point, New York, will use a fuel consisting of a core of thorium dioxide–uranium dioxide with a stainless-steel type 304L cladding. It is proposed to declad the fuel in 4*M* to 6*M* sulfuric acid and dissolve it in 13*M* nitric acid, 0.04*M* sodium fluoride, and 0.04*M* aluminum nitrate (see p. 6). Typical corrosion results are shown in Table IV-4. Of the materials presently being investigated, Illium-R, Nionel, and Carpenter 20 Cb have low rates of dimensional change. However, the latter appears to be sensitive to cracking in stressed areas. It has not been possible to eliminate this cracking completely through solution heat-treatments. The corrosion of Nionel does not appear to be accelerated by cycling in the Sulfex and Thorex environments. In the core dissolution portion of the process, the dissolving medium would be expected to be partially contaminated by sulfate ions from the preceding step. Residual sulfate concentrations in the dissolution environment were found to have no effect on the corrosion of Hastelloy F or stainless steel type 304L.

A rather thorough study on the effect of solution heat-treatments on the corrosion of Carpenter 20 Cb in 6*M* sulfuric acid was made.[14] Anneals were made at four temperatures for two different times; both water quenching and oven cooling were used following the heat-treatment. None of these procedures eliminated the cracking that occurred around stamping marks. In nearly all cases where samples were given a 10-hr solution heat-treatment followed by water quenching, the corrosion rate reduced with in-

Table IV-4 TYPICAL CORROSION RESULTS IN BOILING SULFEX AND THOREX ENVIRONMENTS

Metal	Environment	Corrosion, mils/month	Ref.	Comments
Hastelloy F*	3M H_2SO_4	10	21	
	4M H_2SO_4	20	21	
	4M H_2SO_4	>100	21	Heat-transfer conditions.
HastelloyF,* vacuum melted	3–4M H_2SO_4	16–30	3	Attacked intergranularly.
	3–4M H_2SO_4, Cp†	10	3	
Carpenter 20 Cb‡ welded	6M H_2SO_4	2.4	9,13	Specimen heated to 1950°F, water-quenched; cracking observed in stressed areas.
Carpenter 20 Cb‡ welded	6M H_2SO_4	4.8	9,13	Specimen heated to 1950°F, water-quenched, followed by 1650°F, air cooled; cracking observed in stressed areas.
Carpenter 20 Cb‡ welded	6M H_2SO_4, Cp†	2.9	13	
Carpenter 20 Cb§ welded	6M H_2SO_4, Cp†	0.9	13	
Carpenter 20 Cb§ welded	6M H_2SO_4, Cp†	3.5	13	Exposure to vapor from acid shown.
Illium-R	4M H_2SO_4	0.3	9	Exposure to vapor from acid shown.
Illium-R	6M H_2SO_4	3.6	9	
Illium-R	Initial Thorex			Specimens cracked in stressed areas.
	Final Thorex			
Nionel‡	6M H_2SO_4	0.8–2.0	53	Exposure to vapor from acid shown.
Nionel‡	6M H_2SO_4	2	53	
Nionel§	6M H_2SO_4	0.6	53	
	Initial Thorex	2.9	13	
	Final Thorex	1.1	13	
	Cycled, Sulfex and Thorex	2–4	13	

*Corrosion products, Fe^{+2}, and NO_3^- inhibit corrosion of Hastelloy F in this environment.
†5 to 10 g/liter corrosion products.
‡Corrosion products increase corrosion of Carpenter 20 and Nionel.
§Specimen coupled to dissolving stainless steel type 304.

creased exposure. Specimens which had been oven-cooled regardless of heat-treatment time or those that had been water-quenched after a 2-hr solution heat-treatment showed increased corrosion with time.

Metals still being considered in scouting experiments[14] for the Sulfex-Thorex processing include Illium-98 (an extra low carbon and low iron modification of Illium-R), Haynes-21, Haynes-25, S-816, S-590, and Inconel-700. Rates on Illium-98 ranged from 1 to 3 mils/month for both process environments. All others were not acceptable in the Sulfex dissolution process because corrosion rates exceeded 50 mils/month.

It is proposed to declad stainless-steel fuels in a mixture of nitric and hydrofluoric acid (Niflex process). Typical cores include stainless steel–uranium dioxide mixtures. The latter would be dissolved in an aqueous solution of nitric acid, hydrofluoric acid, and aluminum nitrate. A pilot-plant dissolver and condenser is being fabricated and installed at Hanford;[3,15] vacuum-melted Hastelloy F is being used as the material of construction. An earlier report[3] indicated that some difficulties were being experienced with penetration, undercutting, and weld cracking. However, a more recent report[15] indicates that no weld cracking was observed. Results of recent corrosion tests on Hastelloy F and other candidate materials in the Niflex environments are shown in Table IV-5.

Base metal corrosion rates on the vacuum-melted Hastelloy F used for the construction of the dissolver have shown that rates of attack are 50 to 100 per cent higher than those obtained earlier on small sample specimens. This is true of both Niflex and Sulfex environments.[15]

Fused-salt Volatility Process

By using volatility processing methods, zirconium matrix fuels are dissolved in a molten salt medium and converted to their respective fluorides by anhydrous hydrofluoric acid. The resulting homogeneous salt is subjected to a stronger fluorinating medium such as fluorine, where uranium is converted to the volatile hexafluoride and recovered in a condenser. A corro-

Table IV-5 TYPICAL CORROSION RESULTS IN NIFLEX SOLUTIONS

Metal	Environment	Corrosion, mils/hr	Ref.
Nionel	1M HNO_3-2M HF, boiling	200	21
Incoloy 804	1M HNO_3-2M HF, boiling	200	21
Carpenter 20	HNO_3-HF-$Al(NO_3)_3$ [Al : F > 1]†	<2	3
S.S. 304L*	HNO_3-HF-$Al(NO_3)_3$ [Al : F > 1]†	<2	3
Hastelloy F	HNO_3-HF-$Al(NO_3)_3$ [Al : F > 1]†	<2	3

* Corrosion of S.S. 304L increases substantially when Al : F ratio is less than 1.

† Temperature and composition not indicated but are typical of core dissolvent.

sion program on the dissolution step of the process is well under way at Battelle Memorial Institute (references 9, 13, 14, and 54). A review of ANL's program to June 1958 was included in a Geneva Conference paper. Table IV-6 includes a tabulation of some of the more important results from these sources as well as some of the more recent ANL data. The bulk of BMI's efforts have been on nickel-molybdenum alloys such as Hastelloys B and W, INOR-1, and INOR-8. In general, the severest attack has been found at the interface when undiluted hydrogen fluoride has been passed through the melt. However, some anomalous results have been reported. Strips of Hastelloy W, for example, have severed at the interface while other Hastelloy W components remained intact. Dilution of the hydrofluoric acid with 2.4 wt.% hydrogen has a marked inhibiting effect on the interface corrosion. Rates of dimensional change at the interface were as low as 0.2 mil/month for specimens of INOR-8, and no intergranular attack was observed. In contrast to ANL experience, specimens which were exposed to the alternate contacting of gas and liquid phase were not attacked at high rates. These differences may be due to the geometrical configurations of the respective tests plus gas density and distribution on the metal surfaces.

The result included in Table IV-6 on molybdenum resulted from a test directed toward selection of materials of construction for a volatility processing method on LMFR core fluid. The molybdenum was exposed simultaneously to bismuth, equimolar sodium fluoride–zirconium fluoride, and anhydrous hydrogen fluoride; the latter was bubbled through both liquid phases. Because of the manner in which the tests were conducted, the results are applicable to the dissolution scheme for zirconium matrix fuels.[29]

A comparison of four selected materials was made in a series of tests directed toward the second step (fluorination) of the process.[55] The metals included "L" nickel, "D" nickel, Hastelloy B, and INOR-1. The severest attack occurred at the molten salt–fluorine interface. Results for both dimensional change and intergranular attack are shown in Table IV-7. The significant result obtained is the relative immunity of the nickel-molybdenum alloys to intergranular attack. Dimensional changes of all metals were reasonably comparable. A second conclusion reached during the course of these tests was that the corrosion of Hastelloy B decreased with

Table IV-6 TYPICAL CORROSION RESULTS IN HYDROFLUORINATED SODIUM FLUORIDE–ZIRCONIUM FLUORIDE

Metal	Exposure	Salt comp., % NaF*	Temp., °C	Corrosion, mils/month: Dimensional change	Corrosion, mils/month: Intergranular	Ref.
INOR-1	Gas impingement	62	650	0.03		9
INOR-8	Gas impingement	62	650	0.43		9
INOR-1	Interface	62	650	8.7	14.5	21
INOR-8	Interface	62	650	15.9	23.2	21
Hastelloy B	Interface	62	650	8.7	11.6	21
INOR-1	Interface	50†	650	1.3		21
INOR-8	Interface	50†	650	0.2		21
Hastelloy B	Interface	50†	650	0.8		21
Molybdenum	Liquid, vapor, and interface	50	600	0.2		29

* Remainder ZrF_4.

† Hydrogen fluoride diluted with 2.4 wt.% hydrogen.

Table IV-7 TYPICAL INTERFACE* CORROSION IN FLUORINATED SODIUM FLUORIDE–ZIRCONIUM FLUORIDE[56]

Exposure time:	63 hr of fluorine sparge, 153 hr of helium sparge
Fluorine flow rate:	10 g/hr
Temperature:	600°C
Single specimens:	Partially immersed in melt

Alloy	Corrosion observed, mils: Dimensional change†	Intergranular attack‡	Total	Total mils per month§
"L" Nickel	3.2	16.8	20.0	230
"D" Nickel	4.0	5.3	7.5	86
Hastelloy B	2.3	0.5	2.8	32
INOR-1	2.8	0	2.8	32

* Corrosion at interface was greater than that observed in the liquid or vapor phases.

† Determined with micrometer.

‡ Determined metallographically.

§ Assumes linear rate of attack.

exposure time and was nearly proportional to fluorine flow.

A fundamental study of the reaction of fluorine on nickel surfaces has been initiated at ANL.[56] The reaction rate is being monitored by following the consumption of fluorine. Preliminary results indicate a marked decrease in the rate of fluorine consumption with time. To date, it appears that at temperatures of 300 and 400°C a logarithmic rate law holds. At higher temperatures of 500 and 600°C, the fluorine consumption curves followed a parabolic pattern.

A fluidized-bed method for converting uranium tetrafluoride to the volatile uranium hexafluoride is being studied at ANL. Corrosion in the equipment is being monitored by the insertion of sample strips the complete length of the fluid-bed reactor.[56] The corrosion of the portion of the specimen that was in the fluid bed was relatively low being on the order of 1 mil. However, high rates of dimensional change were observed well above the bed in the vapor portion of the reactor. Additional studies are being made.

Experimental work using molten anhydrous ammonium bifluoride ($NH_4 \cdot HF$) indicates that it may be a promising universal dissolvent for reactor fuels containing zirconium, niobium, and other metals.[57] The term presently being applied to the process is Biflex. Scouting corrosion tests in the liquid ammonium bifluoride at 190°C are being made. Among the more promising materials are the nickel base alloys, monel, and Hastelloy C (3 to 7 mils/year) while 18-8 stainless steels are about a factor of 3 higher.

A fused-salt extraction process for bismuth-uranium fuels uses a ternary eutectic of sodium chloride, potassium chloride, and magnesium chloride to which an oxidant (bismuth chloride) is added. Types of corrosion studies used include static tests, rocking-furnace tests, thermal convection loops, and forced convection loops. The basic systems being investigated include the ternary eutectic salt with and without bismuth chloride and the two-phase mixture of bismuth-uranium fuel plus ternary eutectic salt with and without added bismuth chloride. Results indicate[58,59] that the system parameter most strongly influencing the corrosion rates is the concentration of bismuth chloride. In the two-phase system without oxidant, type 446 stainless steel, $2\frac{1}{4}$ chromium–1 molybdenum steel, and molybdenum show the least amount of corrosion. In the salt phase alone, tantalum also appears to be a possible candidate, although some intergranular penetration was observed. In tests in which the bismuth chloride is added to the salt in concentration up to 5 per cent, corrosion is invariably severe. Actual corrosion rates are not indicated.

Pyrometallurgical Processing

In pyrometallurgical procedures the reactor fuel is essentially processed in the metallic molten form. The containment of such fuels as uranium and plutonium above their melting points poses severe problems. In studies being made for application in the LAMPRE (Los Alamos) reactor, tantalum is thought to be a promising material of construction for containing molten plutonium.[60] The purity of the tantalum probably plays an important role in its ability to resist corrosion. Tests have been made recently with a purer grade of material than was previously available. Both corrosion and weldability have been improved. The new metal appears to have reasonable resistance in 500 hr at 650°C, is attacked slightly at 700°C, and is completely penetrated at 800°C. Recent results also indicate that the metallurgical history of the tantalum may be important. The bulk tests made to date have been on tantalum that has been thoroughly annealed. In a single test at 800°C, a heavily worked specimen of tantalum was exposed to the plutonium environment. In contrast with previous results, no attack was evidenced.

The Ames Laboratory has found that yttrium has potential for the containment of uranium-chromium eutectic at temperatures up to 1000°C. A summary of results obtained on this system to June 1958 was included in a Geneva Conference paper.[61] Three tests are reported: a static test at 900°C for 1100 hr; a rocking furnace isothermal test at 925°C for 1000 hr; and a rocking furnace isothermal test at 925°C for 325 hr. A photomicrograph included in the report from the first test shows nearly a complete lack of interaction between the two phases.

It was determined earlier that yttrium could be welded fairly readily. Recently other fabrication problems have become evident.[44] It work-hardens easily and must be carefully annealed at the conclusion of a drawing process. An extrusion technique for the production of yttrium tubing includes the coating of yttrium with copper followed by extrusion and subsequent dissolution of the copper coating. The material requires oxidation protection above 300°C.

Two cermets designated LT-1 (77 per cent chromium, 23 per cent alumina) and LT-2 (60 per cent tungsten (wolfram), 23 per cent chromium, 17 per cent alumina) were corrosion tested in a molten fissium alloy and in molten magnesium–uranium–5 wt.% chromium.[44] Both materials were deeply penetrated by the fissium environment while reasonable resistance to the second environment was evident. Boron nitride which was previously thought to have low corrosion in molten uranium was tested[56] at 1300°C for 24 hr. The boron nitride was severely attacked.

A molten magnesium environment is of interest relative to its potential use as an extractant of plutonium from irradiated molten uranium. The results of a number of dynamic corrosion tests in this environment were reported.[56] Exposures of tantalum to magnesium at 950°C for a total of 30 days resulted in corrosive attack of less than 1 mil. No localized or subsurface attack was observed. Both stainless steel 446 and Croloy-2¼ showed severe surface roughening at temperatures of 800 and 950°C. Calculated dimensional changes for these alloys vary from 30 to 90 mils/month.

Two additional environments of interest in pyrometallurgical processing are zinc–0.5 wt.% magnesium–0.01 wt.% uranium, and cadmium–0.5 wt.% magnesium–1 wt.% uranium. Mild steel, stainless steel types 410 and 430, Croloy-2¼, and GA Meehanite were exposed in the former environment while mild steel was exposed to the second environment.[56] Temperatures were 475 to 485°C. None of the materials tested were satisfactory in the zinc environment while longer periods of exposure are necessary to demonstrate the compatibility of mild steel with the cadmium environment.

Miscellaneous Corrosion

A topical report on the effect of chlorides on the corrosion of stainless steel in nitric acid environments appeared recently.[62] Tests were made in both liquid and vapor phases in a temperature range of 40 to 120°C. Reference nitric acid concentrations were 220 and 800 g/liter while chloride concentrations ranged from 0.15 to 10 g/liter. The most important parameters influencing the rate of localized attack were free acidity, chloride concentration, temperature, and the presence of dissolved oxygen. Vapor-phase specimens suffered considerably greater local attack than liquid-phase specimens. This is attributable to the lack of oxygen in the liquid as compared to complete access of oxygen to vapor-phase specimens. The vapor-phase attack was found to be most severe at 40°C. At low bulk acid concentrations it was determined that chloride volatility is quite low, and hence localized attack under those conditions is also low.

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CORRECTION: In the preceding issue of this Review (Vol. II, No. 1, January 1959) work on degradation of process solvents was erroneously credited to Reference 8 in the Fuel Processing Research and Development section. Actually the information should have been referenced to J. W. Simmons, Summary Technical Report for Period April 1, 1958, to June 30, 1958, NLCO-750. (Confidential AEC report.)

Congressional Hearings

During late January and early February 1959, the Subcommittee on Radiation of the Joint Congressional Committee on Atomic Energy held five days of public hearings in Washington on the nature and extent of radioactive waste-disposal problems. These hearings, which were originally scheduled to be held last June, were designed as a follow-up to the hearings on "Fallout" held two years ago by the same Subcommittee. It was the intent of the hearings to emphasize the technical aspects of the waste-disposal problems and to determine whether the present scale of research and development is adequate to meet the coming needs. The following subjects were covered: nature of wastes, waste management operations, the various research and development programs, and estimates of the future magnitude and economics of waste disposal. The hearings were concluded with a discussion of the role of various federal, state, and international agencies in the regulation of disposal of wastes. Thirty-three experts covering the entire spectrum of scientific disciplines interested in the problem presented 38 oral papers, and approximately 50 papers were received for the record. All sessions were open to the public.

The complete record of the hearings, which will be available in a few months, will represent one of the most comprehensive collections of technical information on the subject of waste disposal that has yet been compiled in one place. A short summary of the hearings will also be published by the Committee, and this should become available in two or three months.

The opening statement was made by Dr. Abel Wolman, of Johns Hopkins University, who also provided a summary later in the hearings. Some of the points brought out in that summary were:

1. The wastes encountered fall into two classes, which, if not sharply delineated, at least do have major differences in their nature, in their volume, in their hazard, and in their control. One is low-level waste characterized by very large volume and low activity level; the other is high-level waste characterized by more modest volumes (an accumulation of 60 to 70 million gallons at present) but very high activity levels (up to hundreds of curies per gallon).

2. For low-level waste, the program has been to disperse them to nature with or without treatment as required under a very detailed control and management. This program has been successful to date. The problem may be expected to increase, however, as the industry increases in size.

3. For high-level waste, the practice today is to reduce it in volume, if possible, and to contain or hold it in tanks while proceeding with research and development directed toward reducing it even further in volume and toward putting it into such state that it can be handled and controlled safely for indefinite periods in the future.

4. It will always be necessary to use the diluting power of the environment to some extent in handling low-level waste. The cost of "absolutely" processing all these large volumes would be prohibitive. Since the release of small amounts of high-level waste would use up large amounts of environmental dilution power, the reservation of this capacity for the low-level waste where it is needed becomes another reason (in addition to protection of man and other biota) for containing the high-level waste.

5. Tank storage was admitted by all not to be an "ultimate" solution. However, it was emphasized that current operations are safe, and although they are expensive in absolute figures, they are low in relation to total nuclear power costs (or value). It seems likely that temporary (2 to 10 years) tank storage will be a part of an ultimate system to allow decay of fission heat producers before final disposal is practiced.

6. The following suggestions were presented for final disposal: (a) conversion to solids by one of several methods, (b) storage of solids in selected geological strata with major emphasis on salt beds, (c) disposal of liquids into geological strata, either deep wells or salt beds, and (d) disposal of liquids or solids into the sea. There was not complete agreement on the best course to follow, but perhaps the most enthusi-

asm exists for conversion to solids and storage of these in salt mines. The least enthusiasm exists for disposal of high-level wastes in the sea.

7. It was generally agreed that separation of specific fission products (in particular Sr^{90} and Cs^{137}) and their industrial utilization would not affect the waste-disposal problem.

8. We are confronted with a necessity for long-term research and development programs. By long term, we mean that they may extend into generations. This emphasis is made because a short-term budgetary aid to research and development in this very important field, which extends only a year or two, is not likely to produce the result required.

9. All agreed the problem at present was well in hand and were confident that solutions to the remaining problems of ultimate disposal would be found well ahead of their need.

Operating Experience

Two Russian Geneva papers not included in the last Review give information on methods for handling low-level wastes.[1,2] One describes a pilot plant for treating wastes from a research institution.[1] The process used is ion exchange. They state that a technical and economic comparison of evaporation and ion-exchange methods, both giving satisfactory decontamination factors, has shown that evaporation methods are approximately twice as expensive as ion-exchange methods.

Wastes of biophysical laboratories and laundries are separated in a special group which is subjected to primary settling, treatment with activated sludge, and then to secondary settling. These wastes are then mixed with other wastes and are subjected to preliminary decontamination (coagulation, clarification, and filtration) after which they are directed into intermediate storage tanks where their activity is measured. Finally they are subjected to ion-exchange treatment and drained off into natural water basins.

The coagulating treatments remove from 50 to 85 per cent of the radioactivity depending upon the coagulating agent and the dose rate. The ion-exchange treatment is a two-stage decontamination using successively cation- and anion-exchange resins. They report decontamination factors of 10^4 to 10^5. The resins used are specified with Russian trade names. The resins are regenerated with three bed volumes of acid and alkali. Solids from the various processes are centrifuged to reduce their volume, and they are then mixed with "putso-lanian" cement. Before it becomes solid, the mass is discharged into graves whose bottoms and walls are given special treatment to make them waterproof. Effluents discharged to natural waterways meet tolerance requirements. The volume of the solids disposed to the ground is less than 0.1 per cent of the initial wastes [*sic*].

The second paper describes a somewhat similar plant.[2] Low-level waste is first collected in a 12-hr holding tank. It then goes to a mixer where 100 mg/liter ferric sulfate and sufficient caustic soda are added to give a pH of ~10. The waste then goes to a settler and a quartz filter, following which it goes to a cation- and an anion-exchange column. The effluents thus purified are discharged into a river. The wash waters from the filters are recirculated into the process.

The sludge from the settler is periodically drained off for dehydration and burying in a special graveyard with a draining bottom. The graveyard is a pit, 3 to 4 meters deep, dug in the ground with inclined draining sides and consists of two compartments. The bottom and the sides have draining facilities and a filtering layer of quartz sand. A light roof is erected over the pit in order to take advantage of winter temperatures for improving the structure of the sludge and to prevent the radioactive dust from spreading into the atmosphere. When the graveyard is filled, it may be covered with soil or cemented for reliable shielding.

The degree of decontamination achieved at various stages of the process is shown in Table V-1. There is 0.6 m^3 of sludge from every 100 m^3 of treated water per day as a result of decontamination of the radioactive effluents; thus a total concentration of 160 fold is attained.

Table V-1 DECONTAMINATION FACTORS FOR VARIOUS PROCESSING STAGES[2]

Purification stage	General decontamination factor	The factor of decontamination from strontium
Settler	10	3
Quartz filter	*	*
Cation resin	40	1,000
Anion resin	100	*

*No data given in reference.

Final Disposal Methods

The results of extensive study of the movement of individual fission products in sand, as a consequence of disposal operations to ground at Chalk River, have been published.[3] The segregation of the different fission products from each other (although considerable overlapping occurs) is dependent on the nature of the waste (acid of neutral), the chemical form of the fission-product ions, and the nature of the soil itself. The rate of movement of the important fission products disposed in dilute neutral wastes in the order of decreasing movement is ruthenium ≫ strontium > cerium > cesium. For acid waste disposal, at least within a period of two to three years after disposal, the order is strontium = ruthenium > cerium > cesium. After the waste has moved to an extent where the effect of the acid is no longer present, the order should revert to that of the dilute neutral wastes, and ruthenium would move more rapidly than strontium. Cesium moves least quickly in Chalk River soil because it is tightly bound in both the sand fraction and the silt and clay fractions. Ruthenium in anionic form in dilute neutral wastes probably moves at or near the rate of ground water movement. In neutral wastes it is believed that cerium behaves as a cation in the exchange complex and that it enters into precipitation reactions. For both reasons it would be retarded with respect to strontium movement.

It is concluded that large disposals of acid wastes into the soil at Chalk River cannot be recommended as a safe practice, although dilute neutral wastes can be safely disposed on a limited scale if prudent judgment is used in consideration of all factors involved.

A subcommittee of the American Petroleum Institute has been considering the problems of disposal of wastes in deep wells. A report[4] from this subcommittee has stated some of the following conclusions:

1. The disposal of radioactive waste from fuel reprocessing is an element in the cost of atomic power. Although safety is the paramount consideration in the selection of waste-disposal methods, cost is the factor that will govern the choice of safe disposal processes.

2. Radioactive waste can be disposed of safely by injection, through deep wells, into porous rocks. There is, obviously, a limit to the amount and activity of waste that can be stored in any particular formation without danger. This limit cannot be accurately determined on the basis of available information, but the data required for estimating the safe storage capacity of a reservoir can be obtained experimentally.

3. Major problems in the disposal of radioactive waste through deep wells will be those of confining the waste, dissipating the heat generated, and protecting the disposal system against damage by corrosion or radiation. These will present difficulties, but no insurmountable obstacles are indicated.

4. A disposal plant might comprise, in addition to the injection wells, a number of auxiliary wells which serve various functions, with facilities for chemically treating, filtering, and storing waste and diluent water. Although reliable cost estimates cannot be made on the basis of information now available, preliminary consideration suggests that the cost of disposal might run less than a dollar per gallon of high-level undiluted waste.

5. A modest program of laboratory work and theoretical study would clarify many of the problems. If such a study confirms the preliminary conclusion that deep-well disposal might be economic under favorable circumstances, a concurrent program of field testing and exploration should be the next phase of the development of the process to be undertaken.

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In addition to developments in the production of final products (metals and compounds of uranium, plutonium, and thorium) from reprocessed fuel solutions or from uranium hexafluoride, this section will from time to time report on significant developments in the production of refined uranium and thorium from ores or concentrates.

Production of Refined UF_6 from Ore Concentrates

An important new process for the production of gaseous-diffusion grade uranium hexafluoride from uranium ore concentrates is ready to go into production in a 5000-ton per year plant recently completed at Metropolis, Ill. This new Allied Chemical Corporation plant will convert ore concentrates to uranium hexafluoride by hydrogen reduction, hydrofluorination, and fluorination in fluidized-bed reactors (see Fig. 13). Impurities in the uranium hexafluoride are removed by fractional distillation. By avoiding the solvent extraction and aqueous purification methods currently in use at uranium refineries, a considerable economic advantage is expected.

The new process is based on development studies performed at Argonne National Laboratory.[1–3] In this work, ore concentrates assaying about 70 per cent U_3O_8 were first pelleted by extrusion or briquetting and were then crushed and screened to 30-mesh granules. These were continuously converted into crude uranium tetrafluoride in a pilot plant using 6-in.-diameter, multistage, fluid-bed reactors. (This equipment was described in a previous Review[4] in connection with the production of uranium tetrafluoride from pure uranium trioxide.) In tests with ore concentrates from various sources, the pilot plant operated successfully. Two reduction and two hydrofluorination stages were sufficient for conversion of

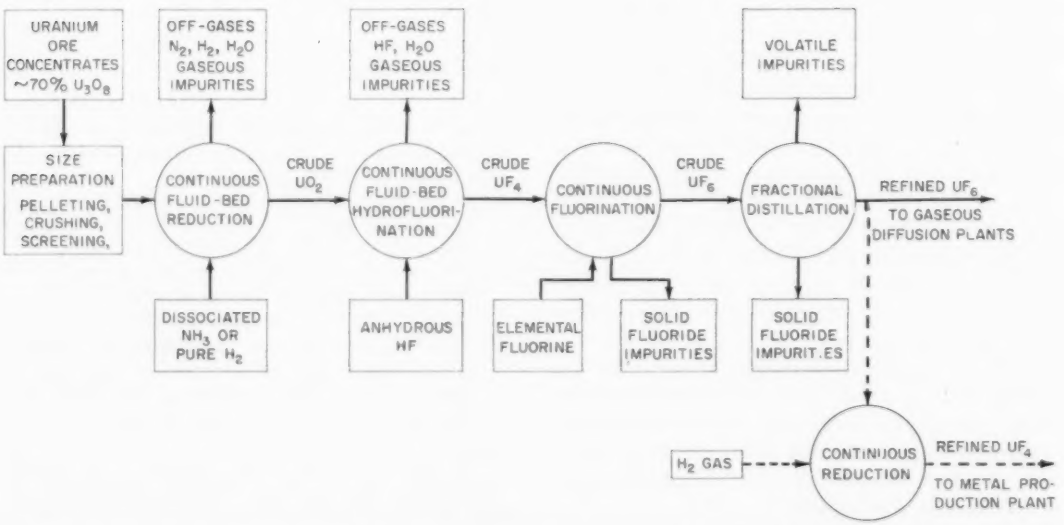

Figure 13—New uranium ore refining process uses fluidization and fractional distillation techniques.[2]

the ore concentrates to uranium tetrafluoride with residence times of 1 to 2 hr in each stage. A large percentage of impurities such as silicon, sulfur, molybdenum, and boron were removed during conversion of the ore concentrates to uranium tetrafluoride.

Fluorination experiments were performed in a 2½-in.-diameter fluid-bed reactor with continuous feeding of uranium tetrafluoride. The gaseous uranium hexafluoride product was taken off through a filter and collected in a refrigerated condenser. Pure uranium tetrafluoride was processed without difficulty as was the crude uranium tetrafluoride derived from acid-leached ore concentrates. Uranium tetrafluoride derived from carbonate-leached ore was more difficult to process because of sintering tendencies and a lower reaction rate. The presence of sodium in this concentrate tends to lower the sintering and melting temperatures of the solid. With the acid-leached material, production rates of uranium hexafluoride of over 100 lb/(hr)(cubic foot of bed) were obtained with a fluidizing gas consisting of 30 per cent fluorine in nitrogen. The rate for carbonate-leached material was about two-thirds that for acid-leached.[5]

Fluorides of vanadium and molybdenum are the only impurities in the crude uranium hexafluoride whose volatilities are such that separation by fractional distillation is required. Solubility studies, liquid-vapor equilibria, and distillation experiments for these impurities have been reported by Allied Chemical Corporation.[6] Vanadium oxyfluoride, which has limited solubility in uranium hexafluoride, was removed by a combination distillation method involving selectively condensing, solidifying, and separating solid vanadium oxyfluoride from the vapor. Vanadium pentafluoride and molybdenum hexafluoride have volatilities higher than uranium hexafluoride and can be separated by conventional distillation.

At the Oak Ridge Gaseous Diffusion Plant, the feasibility of processing ore concentrates directly in the cascade feed plants is under investigation.[7] It has been shown that uranium tetrafluoride derived from ore concentrates containing appreciable quantities of sodium cannot be processed in the existing flame reactors (described in a previous Review[4]) without plugging the unit. Bench-scale studies have shown that the sodium of most concentrates can be reduced to allowable levels by leaching. Larger-scale leaching studies are under way. Other work is directed toward development of selective sorption as an alternate to distillation for removal of vanadium and molybdenum from uranium hexafluoride. Solid sorbents such as alumina and sodium fluoride (in beds 4 to 7 ft deep) have shown appreciable capacity for vanadium but little ability to sorb molybdenum from uranium hexafluoride gas. Other sorbents are being evaluated.

Production of Uranium Tetrafluoride

Thermal Damage Effect

When uranium tetrafluoride is produced from uranium trioxide by reduction and hydrofluorination, the factors that determine the extent of conversion under a particular set of conditions are numerous and interrelated in a complex manner. An attempt to summarize and explain the complex kinetics of these reactions has been made.[8] The effect observed in which higher temperatures are unfavorable to complete hydrofluorination has been called "thermal damage." The term suggests that at high temperatures the outer layer of tetrafluoride on the uranium oxide particles begins to sinter, interfering with access of gas to the unreacted material. Owing to rapid initial reaction rates and high heat of reaction, localized particle temperatures can be considerably above the bulk temperature of the bed. Because of the thermal damage effect, the intrinsic reactivity of an oxide is not necessarily proportional to the amount of conversion to uranium tetrafluoride obtained in a particular process. Thus a very active uranium trioxide may lead to a poor conversion to tetrafluoride under process conditions that produce a satisfactory product from a less reactive starting material.

Preparation from Ores by Wet Methods

The preparation of nuclear-grade uranium tetrafluoride from uranium ores by wet chemical techniques has been the subject of investigations in several laboratories in this country and abroad. An objective is to eliminate the intermediate production of uranium concentrates, thereby reducing capital and operating

costs. An important feature of a successful process is that the final tetrafluoride product be of high bulk density for satisfactory and economical reduction to metal.

A process employing solvent extraction and wet precipitation of uranium tetrafluoride has been studied at the AEC's Raw Materials Development Laboratory.[9] Commencing with a sulfuric acid solution of uranium prepared from either ore or concentrate, the uranium is extracted into a kerosene solution of a long chain secondary or tertiary amine. The amines are characterized by a selectivity for uranium, high extraction coefficients, and good chemical stability.[10] The uranium is stripped from the organic into hydrochloric acid, producing a concentrated solution of relatively high purity. Several solvent extraction flow sheets have been prepared and tested in pilot-plant mixer-settler contactors.

The precipitation of dense uranium tetrafluoride from the hydrochloric acid solution was extensively studied.[11] Hydrofluoric acid and cupric sulfate are added to the strip solution, and the uranium tetrafluoride is precipitated by bubbling sulfur dioxide through the hot solution. Copper acts as a catalyst for the reduction of uranium. The tetrafluoride prepared by this technique ($UF_4 \cdot {}^3/_4H_2O$) has a top density in excess of 3.0 g/cc. Considerable purification occurs in the precipitation step. A sample of tetrafluoride prepared from a Plateau ore sample by this process had impurity concentrations low enough to meet nuclear specifications.

The use of metallic iron for reduction of uranyl ion in chloride solution was investigated by other workers[12] as an alternative to electrolytic reduction in the Excer process.[13] Uranyl chloride solutions were completely reduced in 30 min at 50°C with slight excesses (about 10 per cent) or iron in the form of either sponge, filings, or nails. The final uranous chloride solution contained finely divided carbon from the iron, but this would be removed by filtration. The $UF_4 \cdot {}^3/_4H_2O$ precipitated from this solution by the addition of 10 per cent excess hydrofluoric acid at 90°C had packed densities as high as 2.6 g/cc.

In Japan, development work has been carried out on a process for producing nuclear-grade uranium tetrafluoride directly from Japanese ores[14] containing 0.05 to 0.1 per cent U_3O_8. The process, based on a combination of solvent extraction, electrolytic reduction, and precipitation, has a number of unique features. The ore is leached with sulfuric acid in the usual way, and the clarified uranium solution is treated with a part of the uranium(IV) solution obtained in the following electrolytic reduction operation in order to reduce the iron impurity to the ferrous state. The iron reduction proceeds instantly after the controlled addition of a stoichiometric equivalent of uranous ion. The treated solution is contacted with 0.1*M* di-2-ethylhexylphosphoric acid (D^2EHPA) and 3 per cent tributyl phosphate in kerosene, and the uranium is stripped from the organic phase with 10 per cent sodium carbonate solution. This solution is acidified with sulfuric acid, and the uranyl ion is electrolytically reduced to uranous in a cell with lead electrodes. The uranium(IV) solution is again subjected to solvent extraction using a molar solution of D^2EHPA in kerosene. Uranium tetrafluoride is precipitated directly from the organic phase by contact with a 20 per cent hydrofluoric acid solution. The product is dehydrated in a stream of hydrogen at 300°C. The uranium recovery yield appears to be high, and the uranium tetrafluoride purity is said to be suitable for the production of nuclear-grade uranium metal. Bulk density of the product was not given. Development work is continuing on a pilot-plant scale.

Crude sodium diuranate is one of the major starting materials for the preparation of pure uranium salts. Studies have been carried out in India to prepare reactor-grade uranium tetrafluoride from crude sodium diuranate (a by-product of the thorium industry in India) by a precipitation process.[15] The diuranate was dissolved in nitric acid, and the resulting crude uranyl nitrate solution was treated with ammonium fluoride. Uranium remained in solution as soluble ammonium uranyl fluoride while the insoluble fluorides of thorium, rare earths, and others were filtered off. The filtrate was treated with hydrogen peroxide and ammonia to form the insoluble peroxy complex $(NH_4)_4U_4O_{15}F_6$. The uranium precipitate was filtered, washed, dried, and heated in a current of Freon-12 to get uranium tetrafluoride. On a 5-lb scale, uranium recovery yields of 99 per cent were obtained in the form of the peroxy complex. Conversion to tetrafluoride was 96

per cent complete under some conditions, but the impurity level was somewhat higher than that currently considered acceptable for reactor grade in this country.

Uranium Recovery Operations

Enriched-uranium Scrap

Economical recovery of unirradiated enriched-uranium scrap, generated in fabricating fuel elements, is important to fuel-cycle economy. Some of the recovery and handling procedures in use at the Y-12 Plant at Oak Ridge have been described.[16] Four recovery problems are involved: nuclear safety; health protection; accountability; and nonuniformity of shape, concentration, and composition of the scrap. Safe-geometry closed-vessel equipment, together with hoods and dry boxes, are relied upon for safety. The necessity for ease of accountability of the expensive uranium affects the design of equipment and choice of process. Frequent use of small batch equipment in dissolving operations is required both because of safe geometry limitations and the wide range of sizes of the scrap.

Chemically, the recovery methods used parallel those in aqueous reprocessing of corresponding irradiated fuel elements. Uranium–stainless-steel alloys are electrodissolved in nitric acid, except for the "end pieces" held in the anode clamps which are dissolved in hydrofluoric acid. Uranium-zirconium alloys are dissolved in hydrofluoric acid, and a small amount of nitric acid is added at the end to dissolve tin which is frequently present in the alloy. Uranium-aluminum alloys are treated with caustic which preferentially dissolves aluminum and silica, allowing uranium to be separated as a precipitate. After suitable feed adjustment and complexing of fluoride ions with aluminum nitrate, the uranium is purified by two solvent-extraction cycles with dibutyl carbitol in 4-in.-diameter pulse columns.

Magnesium Fluoride Slag

Magnesium fluoride slag is a by-product from uranium metal manufacture by a thermite type reaction in which uranium tetrafluoride is reduced with magnesium in a refractory-lined steel vessel. The slag contains from 1 to 5 per cent uranium which must be recovered. A recovery process based on fluorination of the uranium to hexafluoride was described in a previous Review.[17] A process based on carbonate leaching has also been developed.[18]

The carbonate process involves the following basic steps: grinding the slag to expose uranium included in slag crystals; air roasting to oxidize the uranium to U_3O_8; leaching with a carbonate-bicarbonate solution containing an oxidant (permanganate) to convert the U_3O_8 to the soluble uranyl tricarbonate complex; further grinding the sal in part of the leach circuit to complete the exposure of uranium to the leach solution; washing to remove residual soluble uranium; and caustic precipitation of uranium for the leach liquor.

Recovery operations were performed in a pilot plant capable of operation at a slag feed rate of about 300 lb per hour. The experimental work demonstrated that under the proper grinding, roasting, and leach conditions the uranium content of magnesium fluoride slag can be reduced to less than 0.05 per cent on a dry basis and that a uranium concentrate can be obtained which is sufficiently low in fluoride to be suitable as refinery feed material.

Recovery of Uranium Hexafluoride from Vent Gases

The vent gases from the uranium hexafluoride manufacturing process at the Paducah, Kentucky plant contain appreciable quantities of oxygen and nitrogen, some hydrogen fluoride and fluorine, and small quantities of valuable uranium hexafluoride. The laboratory tests previously described[4] for recovery of this uranium by absorption in a fluidized bed of uranium tetrafluoride have been expanded to pilot-plant and production scale.[19] The pilot-plant reactor was 6 in. in diameter with a 24-in.-deep bed. Tests in this unit indicated the feasibility of continuous powder feed and withdrawal and showed that regeneration of the exhausted bed with hydrogen would not be necessary if sufficient uranium tetrafluoride feed is available. The capacity of the bed was unaffected by hydrogen fluoride content of 10 per cent in the inlet gas, and the bed temperature was easily controlled at 400 ± 15°F when the fluorine concentration averaged as high as 17 per cent. More than 99 per cent recovery of uranium hexafluoride was effected from a gas mixture

containing approximately 16 per cent uranium hexafluoride and 12 per cent fluorine. Gas velocities between 0.15 and 0.75 fps and powder retention times between 1.6 and 4.2 hr gave satisfactory recovery of both fluorine and uranium hexafluoride. No caking occurred in the fluidized-bed reactor.

A plant-scale adsorber 18-in. in diameter and 36-in. bed depth was installed at Paducah in July 1958. This reactor operates at 400°F, 14 to 16 psia, and is capable of handling 25 to 95 cu ft/min (s.c.) of vent gas. Green salt (75 to 99 per cent uranium tetrafluoride) is fed into the bottom of the fluidized bed by a $2\frac{1}{2}$-in. screw, and spent powder overflows from the top of the bed along with unreacted gases into a cyclone separator. The separated green salt is removed from the cyclone seal leg by a screw conveyor and is transported to the flame reactors in the uranium hexafluoride manufacturing area. The gases to be treated enter the bed of green salt in the absorber through a drilled diffusion plate and maintain the bed in a semifluidized condition. The exhaust gases leave through a cyclone and through two sets of porous metal filter elements in series.

Economics

An economic study has been made[20] of the manufacture of unirradiated uranium fuel materials, including conversion of uranium hexafluoride to uranium metal and uranium dioxide, their subsequent fabrication into fuel elements, and the processing and recycle of accrued scrap. The economic analyses were based on two types of plants referred to as the "Small Plant" and the "Job Shop." The principal difference between these was that the Job Shop had greater flexibility to produce a number of different fuel materials and greater capacity, about six times that of the small plant.

The conclusion reached by the authors was that, in the current period of limited demand and diversified fuels, the versatile Job Shop had considerable advantage arising from its larger-scale, semicontinuous processing and the attendant more favorable distribution of fixed costs and those variable costs not directly proportional to throughput. Further economic advantage would arise from the location of cladding and assembly facilities and radiochemical separation facilities at the same site under a single management to reduce requirements for special auxiliaries, staff personnel, and interplant transport.

There is no single dominating cost factor associated with the manufacture of fuels; rather, there are a number of considerations of nearly equal weight. This situation is likely to prevail until the emergence of uniformity in fuels, under which condition mass production techniques such as extensive use of automatic machine tools for slug machining would be instituted.

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